SHOUT
SHARE
IT

Historic, archived document

Do not assume content reflects current scientific knowledge, policies, or practices.

UNITED STATES DEPARTMENT OF AGRICULTURE

BULLETIN No. 312

Contribution from the Bureau of Soils
MILTON WHITNEY, Chief

Washington, D. C. PROFESSIONAL PAPER November 5, 1915

PHOSPHATE ROCK AND METHODS PROPOSED FOR ITS UTILIZATION AS A FERTILIZER

By

WILLIAM H. WAGGAMAN and WILLIAM H. FRY

CONTENTS

	Page
Introduction	1
Phosphate Deposits of the United States	3
Forms in which Phosphoric Acid is Applied to Soils	8
Processes for Treating Phosphate Rock in the Manufacture of Phosphoric Acid and Phosphatic Fertilizers	8
Processes for the Production of Phosphoric Acid or Soluble Phosphates by Combined Heating and Acid Treatment	12
Double Decomposition by Means of an Alkali, an Alkali Salt, or Alkaline Earth	12
Processes to be Used in Connection with the Iron and Steel Industries	14
Processes in which the Phosphorus or Phosphoric Acid is Volatilized	15
Processes Dealing with the Production of Two or More Fertilizer Elements	17
Processes Dealing with the Production of Available Phosphates by Electrolysis	18
Processes for the Enrichment of Phosphates	19
Mechanical Treatment of Phosphates	20
Miscellaneous Processes for the Production of Available Phosphates	20
Appendix: Classified Tabular List of Patented Processes	21

WASHINGTON
GOVERNMENT PRINTING OFFICE
1915

UNITED STATES DEPARTMENT OF AGRICULTURE

BULLETIN No. 312

Contribution from the Bureau of Soils
MILTON WHITNEY, Chief

Washington, D. C. November 5, 1915

PHOSPHATE ROCK AND METHODS PROPOSED FOR ITS UTILIZATION AS A FERTILIZER.

By WILLIAM H. WAGGAMAN and WILLIAM H. FRY.

CONTENTS.

	Page.
Introduction	1
Phosphate deposits of the United States	3
Forms in which phosphoric acid is applied to soils	8
Processes for treating phosphate rock in the manufacture of phosphoric acid and phosphatic fertilizers	8
Processes for the production of phosphoric acid or soluble phosphates by combined heating and acid treatment	12
Double decomposition by means of an alkali, an alkali salt, or alkaline earth	12
Processes to be used in connection with the iron and steel industries	14
Processes in which the phosphorus or phosphoric acid is volatilized	15
Processes dealing with the production of two or more fertilizer elements	17
Processes dealing with the production of available phosphates by electrolysis	18
Processes for the enrichment of phosphates	19
Mechanical treatment of phosphates	20
Miscellaneous processes for the production of available phosphates	20
Appendix: Classified tabular list of patented processes	21

INTRODUCTION.

The basis of nearly all mixed fertilizers is water-soluble or so-called "available" phosphoric acid, which is produced by submitting bones, a mineral phosphate (apatite or phosphorite), or some other phosphate-bearing substance to a treatment by which the constitution of the original body is materially changed.

Our supply of bones is entirely inadequate to meet the present demands of the fertilizer industry, while apatite has proved objectionable because of the difficulty and expense of mining the mineral and on account of the quantity of fluorine which it contains. By far the greater part of the phosphate fertilizer is derived from phosphorites or amorphous phosphate rock, of which there are enormous deposits in the United States.

For many years the importance of the phosphate industry has been growing steadily. At present the conditions in Europe incident to war have temporarily curtailed the output of phosphate rock, in this country as well as abroad, but on the termination of hostilities the

production of fertilizers will undoubtedly continue its interrupted advance, and the phosphate industry will resume its former activity.

The output of phosphate rock in this country, by States, is given in Table I, and the production, exports, imports, and consumption in the United States for the last 14 years are given in Table II.

TABLE I.—*Production of phosphate rock in the United States.*[1]

[In tons of 2,240 pounds.]

Phosphate.	1910		1911		1912	
	Tons.	Value.	Tons.	Value.	Tons.	Value.
Florida hard rock	392,088	$2,940,660	474,094	$2,953,606	536,379	$3,218,274
Florida land pebble	1,637,709	6,550,836	2,020,477	6,809,007	2,043,486	7,101,186
Total, Florida	2,029,797	9,491,496	2,494,571	9,762,613	2,579,865	10,319,460
South Carolina land rock	185,000	786,250	[2] 169,156	673,156	[2] 131,490	524,760
South Carolina river rock	16,347	57,314				
Total, South Carolina	201,347	843,564	[2] 169,156	673,156	[2] 131,490	524,760
Tennessee	440,699	1,586,516	542,761	1,918,489	443,065	1,710,000
Other States	10,095	40,380	[3] 10,505	39,882	[2] 11,612	46,450
Total, United States	2,681,938	11,961,956	3,216,993	12,394,140	3,166,032	12,600,670

Phosphate.	1913		1914	
	Tons.	Value.	Tons.	Value.
Florida hard rock	485,811	$3,206,343	[2] 309,689	[2] $1,912,197
Florida land pebble	2,043,403	6,334,549	[2] 1,829,202	[2] 5,442,547
Total, Florida	2,529,214	9,540,892	[2] 2,138,891	[2] 7,354,744
South Carolina land rock			[2] 106,919	[2] 415,039
South Carolina river rock				
Total, South Carolina			[2] 106,919	[2] 415,039
Tennessee	434,193	1,628,224	[2]483,203	[2] 1,822,770
Other States	[4] 99,600	[4] 398,272	[2] 5,030	[2] 15,488
Total, United States	3,063,007	11,567,388	[2] 2,734.043	[2] 9,608,041

[1] Statistics collected by Mineral Industry, except as otherwise noted.
[2] Reported by the U. S. Geological Survey.
[3] Idaho, Utah, and Wyoming.
[4] Figures include production of South Carolina and other States not separately mentioned.

TABLE II.—*Statistics of phosphates for the United States.*[1]

[In tons of 2,240 pounds.]

Year.	Production.	Imports.	Exports.[2]	Consumption.	Year.	Production.	Imports.	Exports.[2]	Consumption.
1901	1,483,723	180,714	729,539	934,898	1908	2,375,031	26,734	1,196,175	1,205,590
1902	1,600,813	145,793	802,086	944,250	1909	2,463,766	11,903	1,020,556	1,455,113
1903	1,581,576	153,972	785,259	950,289	1910	2,681,938	19,319	1,083,037	1,618,220
1904	1,874,428	166,090	842,484	1,198,034	1911	3,216,993	16,153	1,246,577	1,980,569
1905	1,933,286	82,072	934,940	1,080,418	1912	3,166,032	28,821	1,206,520	1,988,333
1906	2,052,742	46,228	904,214	1,194,756	1913	3,062,975	26,408	1,338,450	1,724,525
1907	2,251,459	25,896	1,018,212	1,259,143	1914	2,734,043		964,114	1,769,929

[1] Production statistics of 1901 and subsequent years, except 1905 to 1913, are those of the U. S. Geological Survey and are based on marketed products.
[2] Neglecting the insignificant exports of foreign products.

The various deposits of phosphate differ considerably in their geologic occurrence and age, as well as in their physical properties and chemical composition.

The value of a phosphate deposit depends primarily on the grade of the rock, but the mode of occurrence, accessibility, and distance to markets are also factors of the utmost importance in determining its economic value.

The location and character of the American phosphate deposits, their geological occurrence and origin, the methods of mining and extracting the rock, and the cost of production at the various phosphate fields have been described in some detail in a number of papers,[1] but a brief description of the more important deposits is given here in order to compare their possibilities in the economic production of phosphoric acid and soluble phosphates.

PHOSPHATE DEPOSITS OF THE UNITED STATES.

FLORIDA HARD-ROCK PHOSPHATE.

The Florida hard-rock regions lie toward the west coast of the Florida Peninsula and extend from Suwanee and Columbia Counties southward to Citrus and Hernando Counties—a distance of over 100 miles. The mines are reached by both the Atlantic Coast Line Railroad and the Seaboard Air Line Railway, or spurs from these roads. The rock is hauled to the seaports on both the east and west coasts and loaded for shipment abroad.

The rock belongs to the Middle Tertiary period and occurs in irregular pockets embedded in a matrix of sand clay and soft phosphate, the whole usually resting on a limestone. In general the phosphate is a hard, close-grained, nodular, white or cream-colored rock containing from 75 to 80 per cent tricalcium phosphate (bone phosphate of lime), less than 3 per cent of the combined oxides of iron and aluminum, and small percentages of lime carbonate. The remainder of the material is largely silica.

Owing to the pockety nature of the deposits and to the fluctuations in the richness of the phosphatic matrix, the average cost of mining hard-rock phosphate is quite high, but the excellent grade of the product is such that it has heretofore found a ready market in European countries.

FLORIDA LAND-PEBBLE PHOSPHATE.

The land-pebble phosphate area at present productive lies to the south of the hard-rock regions in Polk and Hillsboro Counties.

The mines are reached by the Atlantic Coast Line Railroad and the Seaboard Air Line and the Charlotte Harbor & Northern Railways, or spurs from them.

---

[1] Bul. 69, 76, 81, Bureau of Soils, U. S. Dept. of Agr.; Bul. 18, U. S. Dept. of Agr.

Most of the rock is hauled to Tampa and Port Tampa and there shipped by water to Europe or to the east coast of the United States. The rock belongs to a more recent period than the hard-rock phosphate and is much more regular in its occurrence. As a whole the rock consists of medium-sized, light-gray pebbles somewhat softer than and not of as high grade as the hard-rock phosphates. Its content of tricalcium phosphate runs from 68 to 75 per cent and it contains as a rule less than 4 per cent of iron and aluminum oxides.

The hydraulic method of mining is practiced almost entirely in the pebble regions, and on account of the uniformity of the deposits and the ease with which the material can be handled the rock can be produced very cheaply. Pebble phosphates are by far the most extensively mined of all the American deposits, and up to the year 1914 the output from these fields steadily increased. The consumption of the product has heretofore been about equally divided between this country and Europe.

TENNESSEE BROWN-ROCK PHOSPHATE.

The brown-rock phosphate of Tennessee occurs in the central part of the State, extending in a general north and south direction from the northern to the southern boundary line. The most important deposits so far exploited occur in Sumner, Davidson, Williamson, Hickman, Maury, Lewis, and Giles Counties. The deposits are reached by the Louisville & Nashville and the Middle Tennessee Railroads and the Nashville, Chattanooga & St. Louis Railway. The deposits in Davidson and Sumner Counties have easy outlet to the Cumberland River.

The brown rock is of Ordovician age and in general consists of beds of brown porous plates of varying thickness overlying the original or slightly altered phosphate limestone from which it is derived. Frequently the beds of brown rock are much disintegrated and require special machinery to separate the phosphate from the impurities with which it is mingled. The brown-rock phosphate, as separated by mechanical means, contains from 72 to 78 per cent tricalcium phosphate and from 3 to 5 per cent of iron and aluminum oxides. Practically all of the brown-rock phosphates is now consumed in this country.

TENNESSEE BLUE-ROCK PHOSPHATE.

The important deposits of blue-rock, or Devonian, phosphate in Tennessee lie along Leatherwood Creek, in the western part of Maury County, south and east of Centerville in Hickman County, on both sides of Swan Creek in Hickman County, and in the eastern part of Lewis County near Gordonsburg. The mines are reached by the Louisville & Nashville and the Middle Tennessee Railroads and the Nashville, Chattanooga & St. Louis Railway. The Duck River is

the only navigable stream convenient to the blue-rock fields, and this river has not been used for shipping the rock in recent years. The blue-rock phosphate, as its name implies, is a massive grayish-blue or black rock, composed of flattened ovules and the waterworn casts of phosphatic shells. It weathers on exposure to a rusty yellow.

The beds vary from 1 foot to 4 feet in thickness and are overlain normally by massive blue-black shale. In some localities the blue rock directly overlies the brown phosphate, making the mining of the two types quite profitable.

As a rule the blue rock is of lower grade than the brown, but its content of tricalcium phosphate varies all the way from 60 to 80 per cent, the average content being not far from 72 per cent. The oxides of iron and aluminum are as a rule less than 3 per cent. The cost of mining blue-rock phosphate is about $2.50 per ton.

TENNESSEE WHITE-ROCK PHOSPHATE.

The deposits of white-rock phosphates so far exploited lie in Perry and Decatur Counties, both east and west of the Tennessee River. Some of the deposits in Decatur County are not far from a branch of the Nashville, Chattanooga & St. Louis Railway at Parsons, Tenn., but the only ready means of transportation afforded the present mines in Perry County is the Tennessee River, which is from 4 to 6 miles distant.

The white-rock phosphate is of secondary origin and is more recent than either the blue or brown phosphate. It resembles somewhat the hard-rock phosphate of Florida and some of it is fully as high grade. Picked samples contain as high as 85 to 90 per cent of tricalcium phosphate, with only a small percentage of iron and aluminum oxides. In carload lots the rock will grade from 72 to 78 per cent tricalcium phosphate.

Because of the irregularity of the deposits and the lack of adequate transportation facilities the white phosphates have been exploited only to a very limited extent. It is doubtful whether these deposits will be extensively developed before the more accessible brown-rock and blue-rock fields have been depleted. No mining has been done in these regions in recent years, so that it is difficult to arrive at the actual cost of production. The average cost of producing white-rock phosphate would probably be slightly more than that of mining blue-rock phosphate.

SOUTH CAROLINA PHOSPHATE.

The phosphate area of South Carolina lies along the coast in a belt which is in places fully 20 miles wide, extending from the Wando River in Charleston County to the Broad River in Beaufort County. The rock is of Tertiary age and occurs as nodules and bowlders embedded in a matrix of sand and clay. The beds have an average

thickness of about 1 foot and are mined by means of grab buckets or clam-shell dippers.

The rock as a whole consists of gray nodules of medium hardness, frequently much pitted and the holes filled with clay or calcareous mud, which must be removed by a washing process.

The average grade of the marketed product is about 61 per cent tricalcium phosphate. The average cost of producing South Carolina phosphate is not far from $3.46 per ton, including interest, overhead, etc., and the rock, on board cars at the mines, brings about $4 per ton.

Since the discovery of the higher grade and more cheaply mined phosphates in Florida and Tennessee, the exploitation of South Carolina rock has gradually fallen off. Most of the rock now mined is consumed locally for the manufacture of acid phosphate and double acid phosphate. The latter product, being very rich in soluble phosphates, will stand the cost of transportation.

THE WESTERN PHOSPHATES.

The western phosphate fields are located in southeastern Idaho, western Wyoming, northern Utah, and western Montana. The regions in which the phosphate has been mined or developed so far lie in southeastern Idaho, near the little towns of Soda Springs, Georgetown, and Montpelier on the Oregon Short Line Railroad; along the western front of the Sublette Mountain Range, near Border Station on the Idaho-Wyoming border; at the south end of this same mountain range, about 1½ miles from Cokeville, Wyo., which is also on the Oregon Short Line Railroad; and in the Beckwith Hills in southwestern Wyoming and in northern Utah along the western front of the Crawford Mountains, about 5 miles from Sage Station, Wyo. Practically no development work has been done in Montana, but the phosphate has been recognized near Melrose, Mont., a town on the Oregon Short Line Railroad, and also at Garrison, Philipsburg, and Cardwell on the Northern Pacific Railway from 40 to 70 miles north of Melrose.

The topography of much of the phosphate area is extremely rugged, but many of the beds of phosphate are readily accessible and within easy reach of the railroads mentioned or possible spurs from them.

The western phosphates are original sedimentary deposits laid down when that portion of the earth's surface was submerged in water. The rock is of Carboniferous age and occurs in beds from 2 to 6 feet thick, overlain by limestone and phosphatic shales. It ranges in color from light gray to jet black and in texture from a readily crushed, coarsely oolitic material to a hard massive rock difficult to crush. The rock varies in its phosphate content from 65 to 75 per

cent tricalcium phosphate, with only very small percentages of iron and aluminum oxides. The average cost of mining the western phosphate is from $1.50 to $2 a ton.

Because of their great distance from the fertilizer market, the western deposits have been mined to a very small extent, but the tonnage of high-grade rock in this region far surpasses that of any other area yet discovered.

THE PHOSPHATES OF ARKANSAS.

The phosphates of Arkansas are not generally considered of great economic importance, for, though small bodies of high-grade rock have been found in several localities, the average phosphate content is far below that of the rock mined in Tennessee and Florida.

Mining has been conducted to a considerable extent only in the northern part of the State, in Independence County, about 12 miles from Batesville, a town on the Missouri Pacific Railway. Here the phosphate rock is of Silurian age and occurs in two strata, one directly overlying the other. The upper stratum (from $3\frac{1}{2}$ to 6 feet thick) is the only one considered worth mining, and averages about 55 per cent tricalcium phosphate, with 5 or 6 per cent of the combined oxides of iron and aluminum. No mining has been done in these fields for over a year, since it has been found more economical to supply the demand for phosphate from the richer deposits of Tennessee.

The mining of Arkansas phosphate was conducted in a manner similar to the mining of Tennessee blue-rock phosphate, and the cost of extracting it was approximately the same.

KENTUCKY PHOSPHATE.

Several small deposits of high-grade phosphate rock have been found in the Ordovician limestone in Woodford, Scott, Fayette, and Jessamine Counties, Ky.

The phosphate occurs in thin, close-grained plates, brownish gray in color, and resembles closely the brown-rock phosphate of Tennessee. In order to prepare a high-grade product, the material must be put through a washing process like that employed in the brown-rock fields. The cleaned product varies in its content of tricalcium phosphate from 60 to 75 per cent.

A small amount of development work has been done and a small tonnage shipped from Midway, a little town on the Louisville & Nashville Railroad between Frankfort and Lexington, Ky. So far all the rock sold has been finely ground for direct application to the field.

FORMS IN WHICH PHOSPHORIC ACID IS APPLIED TO SOILS.

There are at present three broad classes of phosphatic fertilizers on the market, namely, water-soluble phosphates, phosphates which are not soluble to any extent in water but dissolve in a solution of ammonium citrate, citric acid, or some other organic solvent, and finally, phosphates which are practically insoluble in the mediums mentioned, but are supposed to yield under proper conditions a phosphatic solution sufficiently strong to produce a marked effect on the crops thus fertilized.

The form in which the first of these classes is usually applied is as monocalcium phosphate, better known as "acid phosphate" or "superphosphate," which is produced by the action of a mineral acid (usually sulphuric) upon phosphate rock. Besides soluble calcium phosphate, however, there are other well-known soluble salts of phosphoric acid, though these are used to a very small extent as fertilizers.

To the second class of phosphates belongs chiefly basic slag, a by-product of the steel industry. Finely ground steamed bone also yields part of its phosphate content to certain organic solutions.

The third class of phosphates includes raw bones and finely ground raw phosphate rock, both of which are quite resistant to the solvent action of the mediums mentioned.

By far the most extensively used of these three classes of phosphates is the water-soluble class, but large tonnages of basic slag are annually consumed for agricultural purposes, particularly in European countries. Most of the acid phosphate produced contains a considerable percentage of "reverted" (so-called) phosphoric acid, which is not soluble in water, but dissolves in ammonium citrate solution.

Because of the undoubted agricultural availability of the phosphoric acid of basic slag, bones, dicalcium phosphate, etc., it has become customary to regard phosphates which are soluble in certain organic mediums as having a fertilizer value nearly equal to that of water-soluble phosphate. Such phosphates therefore are known as available phosphates.

PROCESSES FOR TREATING PHOSPHATE ROCK IN THE MANUFACTURE OF PHOSPHORIC ACID AND PHOSPHATIC FERTILIZERS.

Numerous processes have been proposed and patented for the production of soluble or available phosphoric acid. The claims made for some of these processes are not justified, while many other processes are entirely impractical from a commercial standpoint. Much unnecessary labor has been expended in repeating experiments and in devising processes and apparatus already invented, when a thorough acquaintance with existing methods would have saved both time and money. It is thought, therefore, that classified lists

of the processes devised for the manufacture of phosphatic fertilizers arranged in chronological order, and giving short abstracts of the processes or apparatus employed, the treatment proposed, and the results or new features claimed by the inventors, will aid materially those engaged in researches of this character.

It is impossible in an article of this kind to give more than the briefest abstracts or mention of most of the numerous processes on this subject, but those are described more fully which appear to possess features particularly interesting from either a commercial or scientific standpoint.

For convenience these various methods for treating phosphate rock may be classified as follows:

(1) Acid treatment, which includes the manufacture of superphosphate and phosphoric acid; (2) combined heating and acid treatment; (3) double decomposition by means of a silicate or an alkali; (4) processes used in connection with the steel industry; (5) processes in which the phosphorus or phosphoric acid is volatilized; (6) treatment dealing with the production of two or more fertilizer elements; (7) electrolysis; (8) enrichment or concentration of phosphates; (9) processes and apparatus for the mechanical treatment of phosphates; (10) miscellaneous processes.

ACID TREATMENT.

The production of water-soluble phosphates by the treatment of phosphate rock or bones with sulphuric acid is the oldest and most widely used process. Nitric acid and hydrochloric acid have been tried in place of sulphuric, but the latter has proved itself the most satisfactory, because the calcium sulphate formed is not only a dehydrating agent, but is also only sparingly soluble in dilute solutions of phosphoric acid.

In making superphosphate, ordinary chamber acid (50° B.) and ground phosphate rock are thoroughly mixed in equal proportions by weight and the mass allowed to cure for 24 to 36 hours. The equation showing the reactions in simplest form may be represented thus:

$$Ca_3(PO_4)_2+2H_2SO_4+2H_2O=CaH_4(PO_4)_2+2(CaSO_4.2H_2O).$$

In this case the gypsum formed renders the material dry and pulverulent, and in excellent mechanical condition for mixing with other ingredients in making a complete fertilizer.

The richest superphosphate which can be made, however, by a single acid treatment of the highest grade phosphate mined in the United States (Florida hard rock) contains about 18 per cent of phosphoric acid (P_2O_5). The remaining 82 per cent consists of gypsum, siliceous material, and other impurities. It is obvious therefore, that it is poor economic policy to ship such material long

distances. In order to produce a more concentrated phosphatic fertilizer, the following method is employed:

The ground phosphate rock is mixed with dilute sulphuric acid, and the phosphoric acid thus produced is separated from the gypsum and impurities both by decantation and filtration. The acid is then concentrated by evaporation and sold as such or used to treat another batch of phosphate rock in the production of double acid phosphate, which contains as high as 40 per cent of phosphoric acid (P_2O_5). The equations showing these reactions may be represented thus:

$$Ca_3(PO_4)_2+3H_2SO_4+6H_2O=2H_3PO_4+3(CaSO_4.2H_2O);$$
$$4H_3PO_4+Ca_3(PO_4)_2=3CaH_4(PO_4)_2.$$

A list of the patents on this subject, arranged in chronological order, is given in Table III, Appendix.

Several of the processes cited in Table III, if they accomplish what is claimed for them, should make it possible to produce soluble phosphate more cheaply than by the methods now generally used, or to produce a more concentrated fertilizer, which will admit of shipping it long distances. The following processes have features of interest from either a scientific or an economic standpoint.

The process of Designolle [1] consists in treating phosphate rock suspended in water with sulphur dioxide under pressure, producing thereby a solution of monocalcium phosphate and sulphite of lime—thus:

$$Ca_3(PO_4)_2+2SO_2+2H_2O=CaH_4(PO_4)_2+2CaSO_3.$$

The suspended matter is allowed to settle in some suitable vessel and the solution is boiled with steam to drive off the excess of sulphur dioxide and to precipitate the calcium sulphite. The solution of monocalcium phosphate is then poured off, evaporated to a sirupy consistency, and treated with plaster of Paris to take up the excess of water.

Bergmann [2] claims that dicalcium phosphate free from calcium sulphite is obtained by first mixing phosphate rock with sulphurous acid in the cold, then adding monocalcium phosphate to the solution, and finally boiling the solution to precipitate the dicalcium phosphate and drive off sulphur dioxide.

In the process of Machalske,[3] phosphate rock is subjected to the action of sulphur dioxide in a small quantity of water. The resulting mass is leached with a dilute solution of sulphur dioxide to extract the soluble phosphates, and the residue, which is said to contain a large percentage of calcium sulphite, is calcined to recover the sulphur dioxide, which can be used again.

---

[1] United States Patent No. 196881 (1877).
[2] United States Patent No. 852371 (1907).
[3] United States Patent No. 902425 (1908).

Processes of this type, if practicable, would have an advantage over the one now generally employed in that they produce available phosphoric acid from phosphate rock in a single operation, thus obviating the necessity of first manufacturing sulphuric acid. Experiments in the laboratories of the Bureau of Soils have shown, however, that phosphate rock is very resistant to the action of sulphurous acid or sulphur dioxide, and efforts to obtain complete decomposition of phosphate rock by such treatments were unsuccessful. Further work along these lines, however, seems desirable.

The processes of Glaser [1] have for their object the production of concentrated phosphates by treating phosphate rock with sufficient dilute sulphuric acid to produce phosphoric acid and then using this phosphoric acid as a solvent for more phosphate rock.

They involve the well-known method of making double acid phosphate, a method admirably suited for the treatment of low-grade phosphate rock containing but little iron and aluminum. The equations showing the reactions taking place in this process have already been shown on page 10. The product usually requires artificial drying, since it contains but little sulphate of lime. The patents of Glaser have now expired.

In order to produce a dry pulverulent product, Memminger [2] proposes to mix calcium fluoride or fluorite with phosphate rock and then treat the mixture with sulphuric acid. The generation of gaseous compounds of fluorine, he claims, renders the acid phosphate porous and thus facilitates the escape of moisture from the hot mass.

While this procedure would no doubt produce a high-grade acid phosphate, the poisonous nature of the fumes evolved during the curing of the acid phosphate would make it objectionable to employ such a method either in the vicinity of towns or in a farming country. Moreover, it is questionable whether the extra quantity of acid required to act upon the fluorite would not offset the advantages gained. This patent expired in 1908.

Hoyerman [3] devised a process to economize on the quantity of acid required to produce available phosphoric acid. His process consists in adding to phosphate rock a quantity of sulphuric acid sufficient only to convert it into dicalcium phosphate, a product which has practically the same trade value as monocalcium phosphate.

Such a process, while theoretically possible, presents difficulties in actual practice. The quantity of ordinary sulphuric acid required is hardly sufficient to mix intimately with a large bulk of ground phosphate, and, therefore, the resulting mass is apt to contain a considerable percentage of so-called unavailable phosphoric acid, owing to the fact that some of the phosphate rock has not been acted upon.

[1] United States Patents Nos. 389566 (1888), 417820 (1889), 459575 (1891).
[2] United States Patent No. 445567 (1891).
[3] United States Patent No. 736730 (1903).

The processes of Schlutius [1] and Bretteville,[2] in which nitric acid is employed as a solvent instead of sulphuric acid, are of interest because calcium nitrate and soluble calcium phosphate are produced, both of which are fertilizer materials.

$$Ca_3(PO_4)_2+4HNO_3=CaH_4(PO_4)_2+2Ca(NO_3)_2.$$

Such a mixture is sufficiently high grade to stand the expense of long shipment, but the well-known hygroscopic properties of calcium nitrate form a drawback to its use in fertilizers and would probably necessitate shipping the material in air-tight containers.

PROCESSES FOR THE PRODUCTION OF PHOSPHORIC ACID OR SOLUBLE PHOSPHATES BY COMBINED HEATING AND ACID TREATMENT.

In general, these processes are not very promising, since they involve both acid treatment and the expense of heating the product. A list of the patents under this head is given in Table IV, Appendix.

The process of Scribner [3] appears to be of much interest. It consists in either roasting a mixture of phosphate rock and sulphur or passing sulphur dioxide over highly heated phosphate rock. In either case it is claimed that citrate-soluble phosphate results.

This scheme is similar to two described under "Acid treatment." If it accomplishes what is claimed, much unnecessary time and expense may be saved in the manufacture of available phosphates. From the experience in the Bureau of Soils laboratories, however, it would seem rather difficult to conduct this process so as to effect the complete conversion of the phosphoric acid into an available form.

This patent expired in 1900.

DOUBLE DECOMPOSITION BY MEANS OF AN ALKALI, AN ALKALI SALT, OR ALKALINE EARTH.

All the processes under this head except four depend on heat to effect the conversion of insoluble phosphate into a water-soluble or citric-soluble form. In Table V, Appendix, a list of the various patents on this subject is given.

The object of the processes described below is to obtain a neutral or alkaline product containing available phosphoric acid. Owing to the acid properties of superphosphate there exists among certain farmers considerable prejudice against its use. Fertilizers of the type described below have, as a rule, an alkaline reaction, and therefore are popularly believed to counteract any acidity in the soil.

In the process of Commins,[4] phosphate rock is either heated to redness and then saturated with a solution of sodium chloride or first treated with the salt solution, heated, and then plunged into gas-house liquor. In the more recent process of Lowman,[5] a mixture

[1] United States Patent No. 872757 (1907).
[2] United States Patent No. 1011909 (1911).
[3] United States Patent No. 283426 (1883).
[4] United States Patents Nos. 74799, 78061 (1868).
[5] United States Patent, No. 922494 (1909).

of phosphate rock, sodium chloride, dolomite, and fluorite is made into a paste with water and then baked for 12 hours at 700° F. The inventor claims that citrate-soluble phosphoric acid results, but states that he does not know what reactions take place.

Considering the materials used, however, it is probable that a more basic phosphate containing both lime and sodium is formed on heating such a mixture.

Day's [1] process consists in heating (with or without a potash salt) a natural or artificial mixture of phosphate rock, silica, and limestone to a temperature just above that at which carbon dioxide is driven off. He claims that the resulting product contains phosphoric acid soluble in a 5 per cent solution of citric acid. The length of time of heating required varies between rather wide limits, depending on the materials used and the thoroughness with which they are mixed.

Rocour,[2] Newberry and Barrett,[3] Meriwether,[4] and Landis [5] have devised processes in which double decomposition is brought about by heating a mixture of phosphate rock and sodium sulphate, or phosphate rock, lime, and sodium sulphate. Probably the process under this head which has attracted the most attention is that of Newberry and Barrett. It is understood that the process as worked on a commercial scale differs somewhat from that described in the original patent, but the general plan consists in submitting an intimate mixture of phosphate rock and sodium sulphate to a constantly increasing temperature till a temperature of about 2,800° F. is reached. The clinker formed is then ground, sacked, and sold on the basis of the citrate-soluble phosphoric acid which it contains. It is also said that the final product contains a considerably higher percentage of phosphoric acid than the original mixture, owing to the volatilization of some of the products formed at the high temperatures.

While the reagents required (sodium chloride, sodium sulphate, etc.) to convert phosphate rock into a citrate-soluble form in such processes are comparatively cheap, the expense of maintaining the necessary high temperatures for protracted periods adds considerably to the cost of production. It is claimed, however, that in some of these processes the cost of phosphoric acid per unit is less than it is in acid phosphate.

In order to utilize low-grade phosphates unfit for acid treatment, Wiborgh,[6] Connor,[7] Newberry,[8] and Galt [9] have devised processes in which ground phosphate is mixed with an alkali hydroxide or car-

[1] United States Patent No. 542080 (1895).
[2] United States Patent No. 284674 (1883).
[3] United States Patent No. 1042588 (1912).
[4] United States Patent No. 1058249 (1913).
[5] United States Patent No. 1094857 (1914).
[6] United States Patent No. 601089 (1898).
[7] United States Patents Nos. 931846 (1909). 1042400, 1042401 (1912).
[8] United States Patent No. 978193 (1910).
[9] United States Patent No. 1016989 (1912)

bonate and the mixture heated in a suitable furnace to a bright-red or yellow heat. Newberry also employs lime or limestone in his mix, and Galt uses "lime mud" (a mixture of calcium carbonate and sodium hydroxide), a by-product of the soda industry.

While these processes have not been thoroughly tested in this laboratory a conversion of at least a portion of the phosphate into a citrate-soluble form can undoubtedly be effected by such treatments. The proportions of alkali, lime, and phosphate rock required are such that the resulting product contains a much higher percentage of phosphoric acid than ordinary acid phosphate. For the commercial success of such processes, however, it must be borne in mind that the cost of heating plus the price of the reagents used in the production of a unit of phosphoric acid must not exceed the cost of the sulphuric acid required to produce a unit of phosphoric acid in superphosphates. Payne,[1] in discussing calcination processes, places the cost of available phosphoric acid produced by such processes at about 24 cents per unit.

PROCESSES TO BE USED IN CONNECTION WITH THE IRON AND STEEL INDUSTRIES.

Processes under this head have to do chiefly with the production of tetracalcium phosphate or some other basic phosphate soluble in a 2 per cent solution of citric acid. Because of the high temperature required, these processes can hardly be employed economically except in connection with the smelting industry. A list of the patents dealing with the production of available phosphoric acid along these lines is given in Table VI, Appendix.

In 1884 Thomas[2] devised a process for producing an alkaline phosphate from pig iron high in phosphorus. His plan consists in pouring the molten metal upon an alkali carbonate in a basic Bessemer converter. The resulting slag contains, according to his claim, phosphates of soda which can be separated by lixiviating the mass with water. This patent expired in 1901.

The processes of Reese[3] are also worthy of consideration.

One of his processes consists in adding to the usual furnace charge a certain quantity of phosphate rock to enhance the value of the resulting slag. Another of his processes consists in dephosphatizing the iron or iron ore in two stages. In this way the first slag run-off contains a high percentage of available phosphate. In a third process phosphate rock and basic open-hearth slag are fused together, resulting in the production of available phosphoric acid. If this claim is borne out in actual practice it should be economically

[1] Available phosphates by furnace treatment. Amer. Fertilizer Handbook, pp. 62–64 (1914).
[2] United States Patent No. 301407 (1884).
[3] United States Patents Nos. 412792; 412793 (1889); 714331 (1902).

practicable to manufacture the product by mixing the phosphate rock with the molten slag as the latter flows from the furnace. The heat of the slag could thus be utilized.

The fertilizer value of basic (phosphatic) slag is unquestioned, and it would be practicable to produce large quantities of this material by using phosphatic limestone to smelt siliceous iron ores, but it would be very difficult to overcome the prejudice against using a phosphorus-bearing substance in smelting operations when the chief aim is to eliminate phosphorus from the metal product.

PROCESSES IN WHICH THE PHOSPHORUS OR PHOSPHORIC ACID IS VOLATILIZED.

Processes under this head have been exciting considerable interest in recent years. They are all based on the method long in use for the manufacture of phosphorus and require a high temperature and a furnace which will resist both the temperature and the corrosive effect of the volatile products formed. The main advantage of the processes listed in Table VII is that comparatively pure concentrated phosphoric acid can be obtained from rather impure raw materials.

The first recorded American process for obtaining phosphoric acid in this way is that of Giles and Shearer.[1] Their process of separating phosphoric acid from its impurities consists in passing a current of steam over the acid heated to redness. The distillate condensed and collected in some suitable vessel consists of relatively pure phosphoric acid.

In 1907 Landis [2] described a process for producing phosphoric acid and phosphorus from phosphate rock, which consists in mixing phosphate rock, sand, or a silicate and coke with some binding material, and molding the mixture into briquettes. The briquettes are subsequently placed in an electric furnace and heated. The inventor claims that by this method a more even distribution of the heat is obtained, excessive temperatures can be avoided, and less dust and impurities are carried over with the volatilized phosphoric acid.

The methods of Levi,[3] Washburn,[4] and Haff [5] are three of the more recent processes for the production of phosphoric acid by volatilization. Described in brief, they are as follows:

Levi heats a mixture of phosphate rock and silica or silicate in an electric furnace, claiming that the following reaction takes place:

$$Ca_3(PO_4)_2+3SiO_2=P_2O_5+3CaSiO_3.$$

The phosphoric anhydride which is volatilized is then absorbed in water, producing phosphoric acid (H_3PO_4), and the fused calcium

[1] United States Patent No. 393428 (1888).
[2] United States Patent No. 859086 (1907).
[3] United States Patent No. 984769 (1912).
[4] United States Patents Nos. 1047864 (1912); 1100639 (1914).
[5] United States Patent No. 1084856 (1914).

silicate which remains in the furnace may be converted into a soluble silicate by the addition of an anhydrous salt of potash or soda.

Levi states that it is preferable to have a furnace of such a type that the reacting mass is not in contact with the carbon electrodes, so that the phosphoric acid formed will not be reduced to phosphorus.

Washburn, on the other hand, states that he has carried on experiments like the above on a large scale and claims that unless a reducing agent, such as carbon, be added to the mixture of phosphate rock and silica, the volatilization of phosphoric acid is very incomplete. He heats a mixture of phosphate rock, silica, and carbon until the mass is entirely fused and the phosphorus driven off as such, and also in the form of oxide. He then exposes the gases to an oxidizing atmosphere and converts any phosphorus present to phosphoric anhydride and subsequently to phosphoric acid. He claims that under the proper conditions 90 per cent of the phosphoric acid present in the rock is volatilized.

In a more recent patent, Haff describes a process very similar to the above, but states that pieces of broken carbon should be placed on the bath to form a conducting path of increased current density between the electrodes and thus allow of a higher temperature in the furnace.

Another process of Haff's,[1] as well as a patent taken out jointly by Wilson and Haff,[2] might be included in the subsequent table dealing with processes for the production of two or more fertilizer elements, but since they depend on the volatilization of phosphoric acid they are placed under this head. In these processes a mixture of phosphate rock and feldspar is heated in an electric furnace to a temperature at which both the phosphoric acid and the potash are driven off. The products are then condensed and collected in some suitable manner.

It is generally conceded that cheap hydroelectric power is essential for the commercial success of any of these processes. At present the demand for hydroelectric energy is so great that in any of the localities where it has been developed so far it brings a higher price than can possibly be paid for power in the economic production of phosphatic fertilizers. The enormous energy that can be developed at certain sites, as, for instance, on the St. Lawrence and the Saguenay Rivers in Canada and on the Columbia River in Oregon, energy which, owing to the distance of the power sites from large industrial centers, can not be absorbed through the usual channels, may in the future cause a revolution in the fertilizer industry by making it feasible to produce concentrated phosphates from relatively low-grade materials at considerably less cost than is possible by methods now in general use.

[1] United States Patent No. 1018186 (1912). [2] United States Patent No. 1103910 (1914).

PROCESSES DEALING WITH THE PRODUCTION OF TWO OR MORE FERTILIZER ELEMENTS.

At first glance these methods appear particularly attractive from an economic standpoint, because two or more salable products are obtained by a single operation. Two of the seemingly very promising processes, however, on being tested in the laboratory proved to be commercially impracticable. A complete list of the processes under this head is given in Table VIII, Appendix.

The processes of Bickell [1] and Klett [2] deal with the production of soluble phosphoric acid and potash from phosphate rock and feldspar.

Bickell's process consists in heating in a reverberatory furnace to a light redness for two hours an intimate mixture of 1 part feldspar, 0.5 part phosphate rock, and 3 or 4 parts of lime. It is claimed that both phosphoric acid and potash in available forms are obtained by this treatment.

On testing this process in the laboratory it was found that Bickell's claim was not substantiated, for over 44 per cent of the potash present in the mixture was volatilized upon ignition, and of that which remained in the residue only 9 per cent was water-soluble. While none of the phosphoric acid was volatilized, less than 39 per cent of it was soluble in a 2 per cent solution of citric acid.

Klett's process is similar to that of Bickell and consists in heating to redness for five hours an intimate mixture of 2 parts carbonate of lime, 1 part phosphate rock, and adding for each part of potash (K_2O) in the feldspar 2 parts of calcium fluoride. It is claimed that a soluble silicate of lime and potassium phosphate are thus obtained.

In view of the fact that the percentage of potash in the mixture is relatively small and that the time of heating is very long, it is hardly likely that the value of the product would cover the cost of manufacture. Moreover, the claim that phosphate of potash is formed in the operation is not justified.

The process, however, was tried out on a laboratory scale and results obtained similar to those found in repeating Bickell's method. Nearly all of the potash was volatilized, while less than one-half of the phosphoric acid present in the residue was citric-soluble.

Both the patents of Bickell and Klett have long ago expired.

The processes of McDougall,[3] Terne,[4] Washburn,[5] and Wilson and Haff [6] all deal with the neutralization of the acid in superphosphate by means of ammonia, producing thereby a mixture of gypsum, ammonium sulphate, and calcium ammonium phosphate. These

[1] United States Patent No. 16111 (1856).
[2] United States Patent No. 49891 (1865).
[3] United States Patent No. 135995 (1873).
[4] United States Patent No. 709185 (1902).
[5] United States Patent No. 1100638 (1914).
[6] United States Patents Nos. 1062869 (1913); 1112183 (1914); 1122183 (1914).

processes correct the acidity of the superphosphate which some farmers consider so objectionable, and at the same time enhance the value of the product.

The process of Collett [1] consists in dissolving phosphate rock in dilute nitric acid, and then adding ammonium sulphate to the solution, with the result that lime is precipitated as sulphate, and ammonium phosphate and ammonium nitrate remain in solution. After separating the gypsum, the ammonium salts may be crystallized out by concentration of the solution. The reactions may be represented thus:

(1) $Ca_3(PO_4)_2+4HNO_3=CaH_4(PO_4)_2+2Ca(NO_3)_2$.
(2) $CaH_4(PO_4)_2+2Ca(NO_3)_2+3(NH_4)_2SO_4=3CaSO_4+4NH_4NO_3+2NH_4H_2PO_4$.

This last process is particularly interesting from a commercial standpoint, since it has for its object the production of a high-grade fertilizer containing both phosphoric acid and nitrogen in readily available forms. Where phosphate rock occurs in regions far from the fertilizer markets, the production of a highly concentrated product which will admit of long shipment is essential to the successful development of the mining part of the phosphate industry.

The evaporation of the solutions, however, to the point where the ammonium salts begin to crystallize out would entail considerable expense.

PROCESSES DEALING WITH THE PRODUCTION OF AVAILABLE PHOSPHATES BY ELECTROLYSIS.

Processes under this head are of two types: (1) Those in which the phosphate rock is fused and the electric current passed through the melt; and (2) those in which some water-soluble salt or acid is used as an electrolyte and the ground phosphate rock suspended or dissolved in the solution and the electrolysis performed in the wet way. A list of the patents on this subject is given in Table IX, Appendix.

The process of Palmaer and Wiborgh [2] for the production of dicalcium phosphate is said to have been successfully practiced in Norway where cheap water power is available. The process is as follows:

Perchloric acid and sodium hydrate are produced by electrolizing a solution of sodium perchlorate in a diaphragm cell. Phosphate rock is then treated with the anode solution (perchloric acid) and the resulting solution of phosphate filtered. One half of the cathode solution (sodium hydrate) is then added to this filtrate, resulting in the precipitation of dicalcium phosphate and the formation of sodium perchlorate again. The other half of the cathode solution is treated with carbon dioxide and added to the solution decanted from the dicalcium phosphate precipitate, thus precipitating the lime as carbonate and completely regenerating sodium perchlorate.

[1] United States Patent No. 1058145 (1913). [2] United States Patents Nos. 707886 (1902); 748523 (1903).

The reactions taking place at various stages of the process may be represented thus:

(1) $NaClO_4+H_2O+\text{Electric current}=HClO_4+NaOH$.
(2) $6\ HClO_4+Ca_3(PO_4)_2=2H_3PO_4+3Ca(ClO_4)_2$.
(3) $2H_3PO_4+3Ca(ClO_4)_2+4NaOH=2CaHPO_4+4NaClO_4+Ca(ClO_4)_2+4H_2O$.
(4) $4NaClO_4+Ca(ClO_4)_2+Na_2CO_3=6NaClO_4+CaCO_3$.

This process was designed to treat low-grade phosphates which are not suitable for the manufacture of acid phosphate. Cheap electric power is essential for the commercial success of the process.

PROCESSES FOR THE ENRICHMENT OF PHOSPHATES.

The list of patents given in Table X, Appendix, includes processes for the enrichment of raw or natural phosphates, as well as those which have been chemically treated.

While the writers have placed but five processes under this head, a number of patents classified under other heads could have been included here as well.

The processes of both Ottolengin [1] and Coates [2] have for their object the enrichment of phosphate rock or phosphatic limestone.

Ottolengin advocates the grinding of the phosphate and then effecting the separation of the phosphate particles from the impurities by the difference in their specific gravities, such a separation being made either by a blast of air or by suspending the material in moving water.

Unfortunately, in many of the natural deposits of phosphate, the impurities contained therein have a specific gravity so nearly equal to that of the phosphate rock that a separation on the above basis is usually very incomplete. In the case of the brown-rock phosphate of Tennessee, however, such a scheme is practiced with great success.

By burning, slaking, and subsequently screening phosphatic limestone Coates effects a segregation of the coarser and more phosphatic particles. This process, however, is intended primarily to produce a finely divided sterile phosphatic material for subsequent treatment.

Pratt's [3] process for the enrichment of acid phosphate consists, first, in adding sufficient lime to the superphosphate to convert the monocalcium phosphate to dicalcium phosphate, then leaching out the gypsum contained therein with some suitable solvent. The solvent recommended by Pratt is sea water.

---

[1] United States Patent No. 86574 (1869).
[2] United States Patent No. 971830 (1910).
[3] United States Patents Nos. 1014254, 1014255 (1912).

MECHANICAL TREATMENT OF PHOSPHATES.

The patents listed in Table XI, Appendix, deal with the mechanical treatment of either raw phosphates or the chemically treated product. The first seven processes are primarily intended for the treatment of bones or phosphates to be used in the manufacture of baking powder. The other processes listed hardly require any more detailed descriptions than those given in the tables. All the patents covering these processes have long since expired, and they can therefore be used without payment of royalties.

MISCELLANEOUS PROCESSES FOR THE PRODUCTION OF AVAILABLE PHOSPHATES.

Under the head of miscellaneous are included all the processes which can not very well be separately listed. Many of these processes are on their face practically valueless, while others have features which make it appear they might be successfully employed in the production of fertilizers of some value. A list of the patents under this head is given in Table XII, Appendix.

The process in the above table which has probably attracted the most attention is that of Coates,[1] in which the inventor claims to produce available phosphoric acid and potash from minerals containing these elements by the action of bacteria, which attack and break down the rocks. His process consists in first obtaining a culture by adding breaking-down or decaying rock to a sterilized culture medium. He then inoculates sterilized phosphate rock or feldspar with the culture thus prepared, with the result that the bacteria attack the rock minerals, rendering the phosphoric acid and potash contained therein soluble in the soil solution.

It is understood that field experiments are being conducted to test the fertilizer value of rock treated in this way, but the results of these experiments have not yet been reported.

---

[1] United States Patent No. 947795 (1910).

APPENDIX.

TABLE III.—*Processes for the production of soluble or available phosphates by acid treatment.*

Patent No.	Date.	Patentee.	Reagents used.	Treatment.	Object of process.
16882	1857	Reid, L.	Bone dust, H_2SO_4, liquid manure, absorbents.	The various ingredients are thoroughly mixed with sulphuric acid and allowed to cure.	Production of phosphate nitrogenous fertilizer.
34825	1862	Gallicher, J. M.	Bone black (100), H_2SO_4 (46), liquid animal matter (9).	The various ingredients are thoroughly mixed and allowed to cure.	Do.
38040	1863	Gale, L. D.	Phosphate guano, animal matter, H_2SO_4	do.	Production of concentrated manure.
41428	1864	Harper, L.	Guano, liquid animal matter, H_2SO_4, alkaline salts.	Part of guano is mixed with liquid animal matter, part with H_2SO_4, alkaline salts are added, and the whole thoroughly mixed.	To improve or enrich guano.
41663	1864	Hayes, A. A.	Guano, NaCl, H_2SO_4, animal matter	Ingredients are thoroughly mixed and allowed to cure.	To restore guano.
42006	1864	Liebig, G. A.	Navassa guano, H_2SO_4	The coarse particles of guano are separated from the fine and each part treated separately with H_2SO_4.	To separate and treat guano.
46700	1865	Potts, R. B.	do.	The guano is sprinkled with H_2SO_4	The production of dry pulverulent product.
49831	1865	Liebig, G. A.	Navassa guano, HCl or SO_2	Either HCl or a solution of SO_2 is substituted for H_2SO_4 in the making of acid phosphate.	To use some other mineral acid.
59978	1866	Figanier, A. de.	Phosphate rock, H_2SO_4	Phosphate rock and H_2SO_4 are mixed in a special machine	Improved product due to efficient mixing.
75271 75272	1868	Horsford, E. N.	Tribasic phosphate of lime, HNO_3, H_2SO_4.	$Ca_3(PO_4)_2$ is dissolved in HNO_3. H_2SO_4 is added and $CaSO_4$ thus precipitated. HNO_3 is driven off by heat.	To produce pulverulent acid phosphate.
75325	1868	Wilson, Geo. F.	Bone or its derivatives, niter cake or salt cake, water, steam.	Bones, water, and hot niter cake, salt cake, or both, are placed in a revolving cylinder, and steam is led into the mixture under high pressure.	Production of fertilizer material and distillation of HNO_3 or HCl.
75327	1868	do.	Bones, steam, water, H_2SO_4. Bone charcoal.	Diluted sulphuric acid is first heated in a lead-lined vat, heated by a steam coil, bones and bone charcoal are then added.	Production of $CaSO_4$, $Ca H_4(PO_4)_2$, and $(NH_4)_2 H(PO_4)$.
75336	1868	Wilson, G. F., and Horsford, E. N.	$CaH_4(PO_4)_2$, H_2SO_4, burned bone	Ingredients are mixed and product is leached	Production of acid phosphate.
75338	1868	do.	Bones H_2SO_4	do.	Do.
75339	1868	do.	Phosphate rock, HCl or HNO_3 purified H_2SO_4.	H_2SO_4 is purified and then added to solution of phosphate dissolved in HNO_3.	Production of pure acid phosphate.
76763	1868	Horsford, E. N.	HNO_3, H_2SO_4, bones	H_2SO_4 is added to solution of bones in HNO_3	Do.
86289	1869	Duvall, A.	Phosphate rock, steam, H_2SO_4	Phosphate rock and H_2SO_4 are mixed by means of steam or by air blast.	Improved method of mixing acid and rock.
90367	1869	Lalor, Wm.	H_2SO_4 from refining of petroleum phosphate rock.	Ingredients are thoroughly mixed and product is allowed to cure.	Utilization of waste acid and production of acid phosphate.
113416	1871	Forbes & Paston.	Sewage, phosphate rock, H_2SO_4, $CaCO_3$.	Phosphate rock is acidulated and product treated with sewage.	Improvement in treatment of sewage and production of fertilizer.
125613	1872	Pratt, N. A.	Phosphate rock, slaked lime, H_2SO_4	Phosphate rock is acidulated and then passed through filter press. Filtrate is then mixed with slaked lime.	Production of two cakes of fertilizer.

TABLE III.—*Processes for the production of soluble or available phosphates by acid treatment*—Continued.

Patent No.	Date.	Patentee.	Reagents used.	Treatment.	Object of process.
126904	1872	Pratt, N. A	Phosphate rock, H_2SO_4, lime	H_2SO_4 is mixed with phosphate rock while grinding the latter. Bags are filled with product and pressed lime is added to material coming through bags.	Improvement in treating phosphate rock.
128752	1872	Pratt & Lewis	Phosphate rock, H_2SO_4	H_2SO_4 is mixed with phosphate rock while grinding the latter. Bags are filled with product and soluble P_2O_5 pressed out. Fertilizer salts are added to extract and whole evaporated.	Production of fertilizer and method of making same.
130298	1872	Horsford, E. N	Burned bones, H_2SO_4, water, bone coal, HCl, heat, air, starch.	Burned bones are treated in two charges, the first with H_2SO_4 and the second with HCl. The solutions resulting are mixed and evaporated and taken up with starch.	Production of acid phosphate and absorption of same.
137635	1873	Storck, H., and Lyte, F. M.	Phosphate rock, H_2SO_4, $Ba(OH)_2$ or other convenient form of barium.	Phosphate rock is converted into H_3PO_4 by H_2SO_4. Solution is drawn off and treated with $Ba(OH)_2$. This is filtered and the solution used to produce any desired phosphate.	Production of H_3PO_4 or phosphates free from lime and sulphates.
140559	1873	Tanner, Benj	Phosphate rock, H_3PO_4, lime		Production of acid phosphate of lime.
164457	1875	Jas, A	Phosphate rock, Cl_2, water	Phosphate rock is treated with water saturated with CO_2	Production of H_3PO_4.
173621	1876	Griffith, A. G	Bone dust, guano, manure, H_2SO_4	Ingredients are thoroughly mixed and allowed to cure	Improved fertilizer.
196881	1877	Designolle, G. L. G	Phosphate rock, SO_2 (under pressure), plaster of paris, heat..	Phosphate rock is dissolved by SO_2 under pressure, sulphite of lime separated, and SO_2 driven off from solution by heat. Resulting acid phosphate can be treated as desired	Production of acid phosphate and drying same with plaster of paris.
211238	1879	Jugmanson, Jonas	Ground bone, H_2SO_4, CaO	Ingredients mixed and allowed to cure	Production of available P_2O_5.
238240	1881	Lippincott & Lippincott.	Slag (blast furnace), H_2SO_4	The blast furnace slag is thoroughly sprinkled with H_2SO_4	Production of phosphate fertilizer.
276143	1883	Knight, J. J	Phosphates of iron and aluminum, H_2SO_4.	Ingredients are thoroughly mixed and acid extract filtered	Production of H_3PO_4.
278383	1883	Young, J. K	Phosphate rock, night soil, H_2SO_4	Ingredients are mixed, dried, and pulverized	Production of improved fertilizer.
278480	1883	.....do	Guano, night soil, H_2SO_4	.....do	Do.
279445	1883	Schribler, Carl	Basic slag, HCl, lime	Slag is first roasted, then treated with HCl. Milk of lime is then added to the solution.	Production of precipitate containing available P_2O_5.
281635	1883	Koefoed, A. H	Iron or aluminum phosphate, lime or dolomite, acid.	Ingredients are ground, mixed, calcined, and treated with a mineral acid (H_2SO_4, HNO_3, or HCl).	Production of soluble P_2O_5.
283427	1883	Scribner, E. A	Iron or aluminum phosphate, SO_2, steam.	Steam and SO_2 are passed through the heated pulverized phosphate.	Production of available P_2O_5.
301248	1884	Liebig, G., and Gibbons, J. F.	Phosphates containing iron or aluminum, or both, dilute H_2SO_4.	The phosphates and acid are thoroughly mixed and the resulting solution heated.	Production of soluble P_2O_5.
302666	1884	.....do	Phosphates of iron or aluminum, dilute H_2SO_4, other salts.	The phosphate and acid are thoroughly mixed, the solution filtered, dried, and other fertilizer salts are added.	Production of dry fertilizer containing P_2O_5 and other fertilizer elements.
305249	1884	Stillman & Koefoed	Iron and aluminum phosphates, dolomite, H_2SO_4.	The phosphate and dolomite are mixed and calcined, then treated with H_2SO_4.	Production of phosphate which does not readily revert.
322698	1885	Dibben & Dubbs	Solution of $HNaSO_4$, phosphate rock	The $NaHSO_4$ is dissolved in hot water and the solution used to decompose phosphate rock.	Production of soluble phosphate.
389566	1888	Glaser, Chas	Mineral phosphate, H_3PO_4	Phosphate rock is dissolved in H_3PO_4. The resulting solution is used to treat a fresh batch of phosphate rock.	Production of concentrated phosphate fertilizer.

407240	1889	Powter, N.	Redonda phosphates, animal matter, H_2SO_4.	Ingredients are thoroughly mixed and allowed to cure.	Production of improved fertilizer.
407241	1889	do.	Guano, animal matter, H_2SO_4, $CaCO_3$.	Ingredients are mixed thoroughly and allowed to cure.	Production of an improved dry fertilizer.
417820	1889	Glaser, Chas.	Phosphate rock, H_3PO_4.	Finely ground phosphate rock is treated with H_3PO_4 and allowed to cure.	Production of double acid phosphate.
418259	1889	Winssinger, C. E. D.	Phosphate of lime, H_2SO_4, Na_2SO_4, lime, heat.	Acid phosphate or H_3PO_4 is produced by the action of H_2SO_4 on $Ca_3(PO_4)_2$. The solution is treated with Na_2SO_4, giving NaH_2PO_4. Addition of Na_2CO_3 gives Na_2HPO_4 and precipitates iron and alumina, which is filtered off. Milk of lime is then added to the solution and the whole filtered.	Production of precipitated phosphates of iron alumina, caustic soda, and precipitated lime phosphate.
445255	1891	Seal, Wm. B.	Phosphate rock, H_2SO_4, coal dust, animal matter.	Ingredients are thoroughly mixed and allowed to cool.	Production of improved fertilizer.
445567	1891	Memminger, A.	Phosphate rock, CaF_2, H_2SO_4.	Phosphate rock and CaF_2 are ground intimately together and the mixture treated with H_2SO_4.	Production of dry acid phosphate.
459575	1891	Glaser, Chas.	Phosphate material, dilute H_2SO_4.	Phosphate material mixed with dilute H_2SO_4. Solution of H_3PO_4 resulting is used to dilute more H_2SO_4 and the mixture of acid is used to treat more phosphate rock.	Prodution of H_3PO_4 of growing strength without evaporation.
494940	1893	Rissmüller, Ludwig.	Phosphate rock or bones, organic matter, H_2SO_4.	Organic matter is dissolved in H_2SO_4, fat is skimmed off, and phosphate rock or bones added.	Production of improved fertilizer.
496687	1893	Hoffman, P. C.	Phosphate rock, H_2SO_4, external heat.	Ingredients mixed in the usual way and heated.	Rapid production of soluble phosphate.
504453	1893	Meyer, Theo.	Na_2SO_4, H_3PO_4, $CaCO_3$.	Na_2SO_4 is dissolved in H_3PO_4. $CaCO_3$ is added to solution.	Production of Na_2HPO_4 and gypsum.
515708	1894	Gregory, John.	Bone black from oil purification, H_2SO_4.	Ingredients thoroughly mixed and boiled. Grease is skimmed off.	Production of phosphatic fertilizer from spent bone black.
631181	1899	Schüler, G.	Phosphate rock, H_3PO_4, heat.	Ingredients are mixed and boiled, temperature being held below 115° C. Mass is dried, ground, and silted.	Production of double acid phosphates free from pyrophosphoric acid.
655458	1900	Saxl, H.	Phosphatic material, H_2SO_4, H_2O.	Phosphate is thoroughly mixed with acid and allowed to stand; product is then mixed with water and solution decanted. Solution is then used to treat more phosphate.	Production of concentrated phosphate.
657717	1900	Wharton, J. C.	Phosphate rock, NH_4Cl, H_2SO_4, CO_2, lime, heat, water.	$(NH_4)_2SO_4$, and HCl are first produced by treating NH_4Cl with H_2SO_4. The evolved HCl is led into a mass of phosphate rock suspended in water. Phosphate solution is then filtered and evaporated and placed in a closed container into which NH_3 is led from the decomposition of $(NH_4)_2SO_4$ by lime. The lime phosphate is thus precipitated and filtered off. The solution is then treated with CO_2, which precipitates the lime and regenerates NH_4Cl.	Production or separation of precipitated lime phosphate.
683014	1901	Augstadt & Cleaver.	Phosphate rock, garbage, H_2SO_4.	Garbage is treated with phosphate rock at 400° F. Phosphate rock is then thoroughly mixed with product.	Production of improved fertilizer.
690048	1901	Cheeseman, Lewis.	Phosphate rock, $NaHSO_4$, H_2O, H_2SO_4 or HNO_3, electricity.	Phosphate rock is intimately mixed with $NaHSO_4$ solution, and a current of electricity is passed through the mixture.	Production of monocalcium and dicalcium phosphates.
690049	1901	do.	Phosphate rock, $NaHSO_4$, H_2SO_4.	Phosphate rock is mixed with H_2O and sufficient H_2SO_4 to attack carbonates and fluorides in rock. $NaHSO_4$ is then added and the water removed by evaporation.	Production of a mixture of monocalcium and dicalcium phosphates.
703295	1902	Newport, R. B.	Phosphate rock, garbage, H_2SO_4.	Garbage is first digested to free it from grease, then mixed with phosphate rock and H_2SO_4.	Production of improved fertilizer.
736730	1903	Hoyermann, G.	Phosphate rock (100), H_2SO_4 (30).	Sufficient H_2SO_4 is added to convert phosphate rock to dicalcium phosphate.	Production of citric-soluble P_2O_5.

TABLE III.—*Processes for the production of soluble or available phosphates by acid treatment*—Continued.

Patent No.	Date.	Patentee.	Reagents used.	Treatment.	Object of process.
744128	1903	Strickler, E. H.	Phosphate rock, niter cake, carbonaceous matter.	Phosphate rock and niter cake are digested with water. The liquor is then filtered and mixed with carbon.	Production of trisodium phosphate.
852371	1907	Bergmann, E.	Phosphate rock, water, SO_2, $CaH_4(PO_4)_2$, heat.	Phosphate rock is dissolved in cold H_2SO_3. The solution is then boiled and $CaHPO_4$ precipitated. $CaH_4(PO_4)_2$ is then added to filtrate, resulting in precipitation of more $CaHPO_4$.	Production of $CaHPO_4$.
852372	1907	.....do.....	Phosphate rock, water, SO_2, and P_2O_5, HCl, or H_2SO_4.	Phosphate rock is dissolved in cold H_2SO_3. The free SO_2 is then eliminated by boiling and a mixture of $CaHPO_4$ and $CaSO_3$ is precipitated. After separation, H_2SO_4 or some other acid is added to the precipitate.	Production of $CaHPO_4$ free from sulphites.
872757	1907	Schlutius, J.	Phosphate rock, HNO_3, or other oxides of nitrogen.	Phosphate rock is treated with HNO_3 obtained by oxidizing atmospheric nitrogen.	Production of soluble phosphoric acid.
902425	1908	Machalske, F. J.	Phosphate rock, SO_2, H_2O, heat.	Phosphate rock is subjected to action of SO_2 in presence of small quantity of water. Soluble material then dissolved in water saturated with SO_2. Residue of $CaSO_3$ is then calcined.	Production of soluble phosphate by means of action of SO_2 on phosphate.
997968	1911	Cusatelli, G.	Phosphate rock, H_2SO_4, HNO_3.	Phosphate rock is treated in the usual manner with H_2SO_4 to which a small quantity of HNO_3 is added.	Production of rich phosphate fertilizer which does not readily revert.
1003681	1911	Williams, R.	Phosphate rock, H_2SO_4, refrigeration, NH_3.	Phosphate rock is mixed with H_2SO_4 at low temperatures so that iron and aluminum compounds are unattacked.	Economy in H_2SO_4 and production of soluble P_2O_5.
1011909	1911	Bretteville, A.	Phosphate rock, HNO_3, lime.	Phosphate rock is dissolved in HNO_3. Lime is added to the solution and precipitate separated by decantation or filtration.	Production of phosphate fertilizer containing $Ca(NO_3)_2$.
1020153	1912	Newberry, S. B., and Barrett, H. N.	Phosphate rock, H_2SO_4, HCl, heat.	Phosphate rock is treated with H_2SO_4 and HCl. The solution is filtered from the $CaSO_4$ and evaporated to dryness. HCl is evolved and used again.	Production of $CaHPO_4$.
1034090	1912	Dunham, H. V.	Phosphate rock, H_2SO_4, water.	Ingredients are mixed thoroughly and calcined.	Production of citric-soluble P_2O_5.
1105304	1914	Elliott, W. R.	Phosphate rock (finely ground), H_2SO_4.	Phosphate material is thoroughly agitated by means of an air current and simultaneously sprayed with H_2SO_4.	Production of acid phosphate.

TABLE IV.—*Processes for the production of phosphoric acid by combined acid and heat treatment.*

Patent No.	Date.	Patentee.	Reagents used.	Treatment.	Object of process.
75326	1868	Wilson, G. F.	Bones, heat	Bones are burned	Burning puts bones into better condition for acid treatment.
283426	1883	Scribner, E. A.	Aluminum or iron phosphate, S or SO_2, heat.	Mixture of phosphate and S is roasted, or SO_2 is passed through heated phosphate.	Production of available P_2O_5.
382604	1888	Goodale, S. L.	Minerals containing considerable quantities of hydrated alumina or ferric phosphate or both, carbonaceous material, H_2SO_4, heat.	Mineral is powdered and mixed with carbonaceous material previously moistened with H_2SO_4. Mass is then heated.	Production of available phosphate.
446087	1891	Ruymbeke, J. Van.	Aluminum and iron phosphates, H_2SO_4, heat.	Phosphate is treated with H_2SO_4 as usual, and then heated until it assumes a gray color.	Production of a metaphosphate containing sulphate of both iron and alumina.
446998	1891	do	Phosphate, K_2SO_4 or KCl, H_2SO_4, heat.	Phosphate is powdered, and K_2SO_4 and H_2SO_4 added. The mixture is then heated.	A product which is highly soluble in water, free from stickiness, and nondeliquescent.
462366	1891	Simpson, J.	Tricalcic or dicalcic phosphate, HCl, sulphate of soda, water, heat, caustic lime.	Phosphate is dissolved in HCl and a solution of sulphate of soda added. Supernatant liquor is drawn off and concentrated, the evolved HCl being condensed. The pasty liquor is now heated and then run into water. This solution contains phosphate and chloride of soda which are "salted out" separately. The phosphate of soda is dissolved and treated with caustic lime. Lime phosphate separates out and caustic soda remains in solution.	Production of caustic soda and, if desired, lime phosphate.
995028	1911	Newberry, S. B., and Barrett, H. N.	Phosphate rock, H_2SO_4, heat	Phosphate is pulverized and mixed with H_2SO_4. Mixture is calcined in an oxidizing atmosphere. This decomposes the $CaSO_4$ with liberation of SO_2 and O. Material is then ground.	Production of a citrate-soluble material containing calcium pyrophosphate and free lime.
1024880	1912	Coates, L. R.	Native phosphates, limestone, heat, H_2SO_4.	Phosphate and limestone are powdered and mixed. The mixture is calcined and then slaked with H_2SO_4, only enough acid being used to leave the material as a dry powder.	Production of a fertilizer.

TABLE V.—*Processes for the production of soluble or available phosphates by decomposition with a silicate, alkali, or alkaline earth.*

Patent No.	Date.	Patentee.	Reagents used.	Treatment.	Object of process.
45961	1865	Liebig & Cooper	Aluminum or iron phosphate, lime, soda, or potash.	Phosphate is heated with lime. Resulting $Ca_3(PO_4)_2$ is treated with soda or potash.	Production of an alkaline phosphate.
74799	1868	Commins, John	Phosphate minerals, heat, solution of common salt.	Phosphate is heated and then saturated with the salt solution	Production of soluble phosphate.
78061	1868	do	NaCl solution, gas liquor, phosphate rock.	Phosphate is treated with NaCl solution, heated, and plunged into gas liquor.	Production of soluble or available P_2O_5.
90057	1869	Stewart, David	Phosphate rock, potash solution, lime, gypsum.	Alternate layers of phosphate moistened with caustic potash solution and lime are composted. Gypsum may be added on barreling the mixture.	Production of "the persicator."
102438	1870	Sapp, W. I	Phosphatic guano or bones, etc., water-glass.	Constituents are mixed	Production of water-soluble phosphate.
119994	1871	Prescott, D. W	Bone dust (1,600 pounds), soda ash (300 pounds), water (15 to 20 gallons).	Bone dust and soda ash are mixed and moistened with water. The mass is allowed to remain in a heap for about two weeks and then dried.	Production of soluble phosphate.
123743	1872	Tanner, Benjamin	H_3PO_4, NaCl, heat	H_3PO_4 is treated with NaCl. Moisture and HCl are then evaporated off.	Production of sodium phosphate.
252029	1882	Gibbons & Liebig	Aluminum or iron phosphate, soda or potash salts, carbonaceous matter.	Mixture is burned and acidulated	Method of increasing the availability of P_2O_5.
284674	1883	Rocour, Georges	Phosphatic slag, coal, Na_2SO_4	Reduce phosphate and then roast with Na_2SO_4	Production of Na_3PO_4.
453299	1891	Glaser, Charles	Aluminum phosphate, alkali solution, heat, CO_2, lime.	Phosphate is digested with alkali solution, this being promoted by heat. The resulting solution is separated from the residue and saturated with CO_2, phosphate of alumina being precipitated. Lime is added to the remaining liquid to recover alkali.	Production of citrate-soluble phosphate.
453300	1891	do	Aluminum phosphate, carbonate or phosphate of an alkali, water, heat.	Finely divided phosphate is treated with solution of alkali carbonate, being heated in the meantime. Resultant solution is separated from residue and cooled, phosphate of aluminum being deposited.	Production of citrate-soluble aluminum phosphate.
542080	1895	Day, David T	Phosphate rock containing SiO_2 and $CaCO_3$ (should the rock not contain these they are added), heat, salt of an alkali.	Phosphate rock is heated to a point below fusion but above temperature of decomposition of $CaCO_3$. Addition of a salt of an alkali lowers necessary temperature.	Production of citrate-soluble lime phosphate.
588266	1897	DeChalmot, G	Phosphate rock, electric current, sand, water.	Phosphate is crushed and fused in an electric furnace. The fused mass runs out and falls upon sand. It is then dumped into water.	Production of citrate-soluble phosphate.
589197	1897	Stead, J. E	Natural phosphates, siliceous and calcareous matter.	Materials are melted together	Phosphate soluble in solvents existing in the soil.
598182	1898	Poole, Herman	Native aluminum phosphate, heat, caustic soda solution, aqueous solution of sodium silicate, H_2SO_4.	Phosphate is boiled in caustic soda solution. It is then filtered and the filtrate mixed with sodium silicate solution. Alumina is thus precipitated as silicate. The sodium phosphate remaining in solution is crystallized out. The aluminum silicate is heated with H_2SO_4, yielding aluminum sulphate.	Production of tribasic sodium phosphate and aluminum sulphate.
601089	1898	Wiborgh, J. G	Apatite, carbonate of sodium or potassium or caustic soda or potash, heat.	Mixture is heated	Production of citrate-soluble tetracalcium sodium (or potassium) phosphate.

721489	1903	Wolters, Wilhelm	Phosphorites or bone, silicates of alkaline earths and alkalies, heat.	Materials are melted together	Production of citrate-soluble phosphate.
917582	1909	Strickler, E. H	$NaHSO_4$, phosphate rock, heat	Phosphate rock is dissolved in a solution of $NaHSO_4$ and Na_2SO_4 crystallized out.	Process of separating Na_2SO_4 from H_3PO_4.
922494	1909	Lowman, J. W	Phosphate rock or bones, etc., NaCl, dolomite, fluorspar, heat, water, potash.	Phosphate is pulverized, and dolomite and fluorite are burned and pulverized. All are mixed with NaCl and water. The mass is then heated. Potash is added when the phosphate rock is highly siliceous.	Production of available phosphate.
931846	1909	Connor, J. H	Phosphates, Na or K hydroxides or carbonates, Ca or Mg or Ba hydroxides, water, heat.	Ground phosphate is mixed with alkali, alkaline earth, and water. This mixture is heated and then ground.	Production of available phosphoric acid.
972567	1910	Newberry, S. B	Natural phosphates or bones, etc., phosphoric acid or water-soluble phosphates such as those of Na or K, heat.	Mixture is calcined and ground	Production of citrate-soluble phosphate.
978193	1910	....do	Phosphate rock or bone, lime, soda or potash carbonate as flux, heat.	Materials are mixed, calcined, and ground	Do.
991096	1911	Schröder, Heinrich	Aluminum, iron, and calcium phosphates, Mg or Ca chlorides, water, heat, NaCl.	Phosphate and chloride are mixed and heated with exclusion of air after the principle of fractional sublimation. Above 100° C. the vapors are led into NaCl solution and aluminum sodium chloride is formed. Above 183° C. HCl is formed and condensed. Above 280° C. ferric chloride is formed, which may be decomposed into ferric oxide and HCl by steam. The residue in the furnace contains the alkali earth phosphate formed. If $MgCl_2$ has been used, the phosphate formed is soluble in citrate solution. If $CaCl_2$ has been used, the phosphate must be treated (HCl treatment) to render it soluble.	Do.
995894	1911	Palmaer, W	HCl, NaOH, phosphate rock	Phosphate rock is dissolved in HCl and NaOH added to precipitate.	Production of citrate-soluble P_2O_5.
1002198	1911	Frerichs, F. W	Calcium phosphate, ammonium sulphate, heat, H_2SO_4, water.	Phosphate and ammonium sulphate are mixed and roasted. Ca pyrophosphate is obtained, ammonia being driven off. The pyrophosphate is treated with H_2SO_4 and water, $Ca(PO_4H_2)_2$ and $CaSO_4$ being obtained.	Production of a fertilizer.
1016352	1912	Meriwether, C. N	Natural phosphate, carbonate or fluoride of lime, heat, water, potash granite or magnesia.	Phosphate is mixed with the lime compound, and the mass fused. It is then run into water and ground. Potash-granite or magnesia may be added.	Do.
1016989	1912	Galt, H. A	Lime mud (a mixture of $CaCO_3$ and NaOH obtained as a by-product in the manufacture of caustic soda), phosphate rock, heat.	Lime mud and phosphate are mixed and heated	Production of soluble phosphates.
1025619	1912	Giese, F., and Wolters, W.	Natural phosphate, artificial silicates (or their raw materials, such as acid sodium sulphate, limestone, and sand), heat, steam, air.	Phosphate and artificial silicate are melted together, and the melted mass is finely distributed by a blast of mixed steam and air.	Production of citrate-soluble phosphate.
1042400	1912	Connor, J. H	Phosphate rock or bones, etc., limestone, soda, iron oxide (flue dust) or sodium sulphate, water, heat.	Materials are mixed, and, in a wet state, subjected to a high temperature. It is then ground.	Production of available phosphate.
1042401	1912	....do	Phosphate rock or bones, etc., soda ash or sulphur soda ash, iron oxide (flue dust) as a flux, heat, water.	Materials are mixed and heated	Do.
1042402	1912	....do	Phosphate rock or bones, etc., sodium salts, heat, water, iron oxide (flue dust).	Materials are mixed, heated, and ground	Do.

TABLE V.—*Processes for the production of soluble or available phosphates by decomposition with a silicate, alkali, or alkaline earth*—Continued.

Patent No.	Date.	Patentee.	Reagents used.	Treatment.	Object of process.
1042588	1912	Newberry, S. B., and Barrett, H. N.	Natural phosphates, alkali sulphates, water, heat.	Materials are mixed and heated in an oxidizing atmosphere	Production of citrate-soluble phosphate.
1058249	1913	Meriwether, C. N.	Phosphate rock, lime rock, heat, compound of Na or K, etc. Iron oxide dolomite, may be added.	Phosphate and lime rock are mixed, ground, and heated. Mass is then run out, combined with Na and K compounds, ground, again heated, and reground.	Production of a fertilizer.
1094857	1914	Landis, W. S.	Phosphate rock, Na_2SO_4, water	Mixture is dried and calcined	
1103059	1914	do	Phosphate rock, Na_2SO_4 or Na_2CO_3, water, C.	Mixture is burned while air is being blown through. Product is pulverized.	Production of soluble or available P_2O_5.
1111490	1914	Perino, Josef	Potash containing silicate rock, phosphate rock, $MgCl_2$, heat, steam, water.	Mixture is heated in presence of steam. Product is treated with sufficient water to cool and hydrate the same and leave a dry powder.	
1120917	1914	Downs, W. F.	Finely divided phosphate rock, finely divided silica, heat.	Mixture is heated	Production of citric-soluble phosphate.

TABLE VI.—*Processes to be used in connection with the iron and steel industries for the production of soluble or available phosphates.*

Patent No.	Date.	Patentee.	Reagents used.	Treatment.	Object of process.
284674	1883	Rocour, G.	Phosphatic slag, flux, lime, Na_2SO_4, H_2SO_4, coal or coke, pyrites, H_2O.	The slag is first fused under reducing conditions. (1) The matte is blown in a basic converter with the addition of lime and small quantities of Na_2SO_4. (2) Matte is mixed with Na_2SO_4 and coal and heated in reverberatory furnace in reducing flame, oxidizing flame being used later. Mass is then lixiviated.	Methods of obtaining soluble alkaline phosphates.
301406	1884	Thomas, S. G.	NaCl or KCl, iron containing over 1 per cent P, superheated steam or water gas, Fe_2O_3, H_2O, lime, air, heat.	The alkaline chlorides are blown into the phosphorus iron in a Bessemer converter along with steam, water gas, or other hydrogen-yielding substance. Resulting slag is lixiviated and lime added to the solution.	Production of precipitated phosphate of lime from phosphorus-bearing iron.
301407	1884	do	Molten pig iron containing P, Na_2CO_3, $NaNO_3$, lime, H_2O, heat.	Molten metal is poured upon an alkali carbonate in a basic Bessemer furnace. More Na_2CO_3 is introduced by the blast. The slag is then run off and lixiviated.	Production of alkaline phosphate from phosphorus-bearing iron.
306664	1884	Thomas, S. G., and Twinman, T.	Slag containing iron oxide and P_2O_5, HCl, oxidizing agent, lime, H_2SO_4, H_2O, heat.	Slag is first treated with HCl, ferrous oxide in solution is then oxidized by Cl or some other agent. Powdered chalk is then added to the solution, precipitating the iron as ferric phosphate. This is filtered and treated with H_2SO_4. The H_3PO_4 is then either separated or the mixture used in the manufacture of acid phosphate.	Production of H_3PO_4 from phosphatic slag.
312904	1885	Scheibler, Carl	Slag (phosphatic), slow cooling	Phosphatic slag is allowed to cool very slowly	Segregation of P_2O_5 near surface of mass.
324471	1885	Imperatori, Luige	Phosphatic slag, Na_2SO_4, C, CO_2	Slag is melted with Na_2SO_4 and C. Resulting mass is then treated with CO_2 and lixiviated.	Production of Na_2HPO_4 and Na_2CO_3.

353825	1886	Scheibler, Carl	Slag (phosphatic), heat, H_2O, lime	The slag is roasted in oxidizing flame, ground, and treated with HCl. Milk of lime is added, fractionally precipitating (1) phosphates of iron, (2) the alkaline earth phosphates. The phosphates of iron are then again roasted with lime, giving phosphates of lime.	Production of phosphates of lime from slags containing iron phosphates.
361656	1887	Twynam, Thos	Phosphatic iron, Na_3PO_4, Na_2CO_3	Na_3PO_4 is added to molten phosphatic pig iron, and Na_2CO_3 is subsequently added.	Production of soluble P_2O_5.
372087	1887	Reese, Jacob	Basic phosphatic slag, magnet	Slag is pulverized and the iron separated by magnet	Production of available P_2O_5.
412792	1889	do	The usual furnace charge, with the addition of phosphate rock.	The phosphate rock is oxidized at high temperature in the presence of lime. The slag is then withdrawn and slowly cooled.	Production of $Ca_4P_2O_9$ or available P_2O_5.
412793	1889	do	Phosphatic iron, CaO, heat	A mixture of phosphatic iron and CaO is charged in basic Bessemer convertor and slag withdrawn before iron is completely dephosphatized. Fresh lime is then added to charge.	Production of highly phosphatic slag, and subsequent dephosphatization of steel.
535204	1895	Howe, H. M., and Stead, J. E.	Slag, phosphate rock, a metallic base, lime, heat.	Phosphate rock is added to the molten slag in the furnace; lime is added if necessary. Slag is then run out before iron is completely dephosphorized. Slag is comminuted.	Production of tetracalcium phosphate.
550024	1895	Meyer, Emil	Phosphatic slag, Na_2CO_3	Na_2CO_3 is added to molten slag as it issues from furnace	Production of disintegrated slag.
714331	1902	Reese, Jacob	Phosphatic slag, phosphate rock, CO_2, heat.	Phosphate rock and slag are mixed and fused in a furnace in presence of oxidizing flame; gases should be largely CO_2.	Production of fertilizer containing available P_2O_5.
977819	1910	Mehner, H	Iron ore, phosphate rock, oxides of iron, lime, carbon, heat.	Iron ore and phosphate rock are heated in blast furnace. The slag produced is separated from iron rich in phosphorus. The iron is treated a second time with basic materials, giving another highly phosphatic slag.	Production of two highly phosphatic slags and elimination of phosphorus from iron.
1002297	1911	Meriwether, C. N	Iron ore, phosphate rock, lime, heat, salts of Ba, K, Na, NH_4, and Mg may be used or ferrocyanide of potash.	Phosphate rock and iron ore are intimately mixed. Mixture is then heated to redness for 1 hour to 6 hours while being agitated. Fertilizer salts may be mixed with cooled product.	Production of available P_2O_5 which may be mixed with fertilizer salts.
1067224	1913	Slater, O. K	Basic slag, phosphate rock, steam, SO_2, NH_3.	A mixture of slag and phosphate rock is placed in a digester and steam led into mixture. The slag disintegrates. SO_2 is then introduced and then NH_3 gas.	Production of a mixture of soluble and available P_2O_5 and $(NH_4)_2SO_4$.

TABLE VII.—*Processes for the production of phosphorus and phosphoric acid by volatilization.*

Patent No.	Date.	Patentee.	Reagents used.	Treatment.	Object of process.
393428	1888	Giles, W. B., and Shearer, Arthur.	Phosphatic material, steam, heat	Phosphatic material is so treated as to obtain an impure phosphoric acid. This is concentrated and placed in a retort. Here it is kept at a red heat and a current of steam is passed over it. The distillate is condensed.	Process for separating phosphoric acid from impurities.
417943	1889	Readman, J. B	Phosphorus-yielding material in solution, carbon, a flux, electric furnace.	The phosphorus solution is concentrated and carbon incorporated. A flux may be added. It is placed in an electric furnace and phosphorus distills over.	Process of obtaining phosphorus.
452821	1891	Wing, H. H	Phosphate rock, siliceous material, coal or coke, heat.	Phosphate rock is ground, mixed with the siliceous material, and molded into small balls. These are placed in a furnace with coal or coke. On heating volatilization takes place and the fumes are condensed.	Do.

TABLE VII.—*Processes for the production of phosphorus and phosphoric acid by volatilization*—Continued.

Patent No.	Date.	Patentee.	Reagents used.	Treatment.	Object of process.
540124	1895	Ruymbeke, Joseph Van.	Natural phosphate, acid flux, reducing agent, air, heat.	Phosphate is mixed with an acid flux and a reducing agent, and heated in a blast furnace. Air is introduced into the upper part of the furnace to oxidize the phosphorus. The resultant P_2O_5 is carried to a scrubber.	Process for producing phosphoric acid.
689286	1901	De Chalmot, G.	Natural phosphates, silica, heat, moist lime, water.	Phosphate and silica are mixed and heated in an electric furnace. As fast as it becomes molten the mass is removed and brought into contact with a further quantity of silica. It is then dumped into water. Any phosphoric acid volatilized is brought into contact with moist lime.	Production of suluble phosphoric acid.
733316	1903	Duncan, R. K.	Phosphatic material, carbon, tar, hydrogen, heat, water, electricity.	Powdered phosphate is mixed with carbon and tar, the latter serving as a binder. The mixture is placed in an electric furnace. The resultant calcium phosphide is removed and placed in a chamber with hydrogen gas. Water is led in. The resultant phosphorus hydrides are dried and heated.	Production of phosphorus.
789438	1905	Machalske, F. J.	Phosphate rock, alkali-metal chloride (NaCl), carbon, heat, water.	Rock is crushed and mixed with NaCl and carbon. The mixture is heated. Phosphoric chloride is led off and treated with water.	Production of phosphoric chloride or acid and HCl, and carbides of calcium and sodium.
789439	1905	do	Phosphate rock, alkali-metal chloride (NaCl), carbon, nitrogen, water, heat.	Rock is crushed and mixed with NaCl and carbon. The mixture is smelted. Phosphoric chloride is given off and may be treated with water. Nitrogen is brought into contact with the charge in the furnace.	Production of phosphoric chloride or acid, HCl, and cyanamids.
789440	1905	do	do	As above, with the addition that the calcium sodium cyanamides are smelted with carbon and sodium carbonate.	As above, with the production of sodium cyanide in addition.
859086	1907	Landis, G. C.	Phosphates, sand or silicate, coke, binding material, heat.	Phosphate, sand, and coke are crushed independently of each other and calcined. They are then ground, mixed, and formed into briquets with the binding material. The briquets are then fed into an electric furnace.	Process which makes excessive temperature unnecessary, prevents dust being carried over, and gives a more even action of the heat.
862092	1907	Morehead, J. T.	Phosphate rock (calcined bones, etc.), carbon, heat.	Phosphate and carbon are beated in a furnace, and the phosphorus distilling over is condensed.	Production of phosphorus and calcium carbide, and CO.
862093	1907	do	do	do	A material containing calcium carbide and phosphide.
902157	1908	Maywald, F. J.	Phosphate rock, electric current, air.	Electric current is passed through phosphate rock in a furnace to which air is admitted. P_2O_5 fumes condense in a hood.	Production of P_2O_5.
984769	1911	Levi, Giorgio	Natural calcium phosphates, heat, SiO_2, etc., anhydrous sodium salt, mineral colors.	Phosphate mixed with SiO_2 is heated in an electric furnace. Phosphoric anhydride escapes and is collected. Sodium salt added to the calcium silicate remaining in the furnace gives soluble sodium silicate. Mineral colors added to the silicate produce valuable colored material.	Production of phosphoric anhydride and calcium silicate, sodium silicate, and these latter colored.

1018186	1912	Haff, M. M.	Feldspar, calcium phosphate, heat	Feldspar and phosphate are heated together in a furnace. Phosphoric acid and potash are volatilized together.	Production of potassium phosphate and a slag which may be used for glass making.
1044957	1912	Washburn, F. S.	Phosphate, silica, and carbon	This invention relates to an electric furnace	Production of phosphoric acid.
1047864	1912	do	Natural phosphates, SiO_2, carbon, air, heat, water.	Phosphate, SiO_2, and carbon are heated together in an electric furnace. Air is introduced to oxidize the phosphorus driven off. P_2O_5 is treated with water.	Do.
1084856	1914	Haff, M. M.	Phosphate rock, silica, coke	Materials are heated in an electric furnace	Production of phosphorus and P_2O_5.
1100639	1914	Washburn, F. S.	Phosphate rock, silica, carbon	Materials are heated first by fuel, then by electricity	Production of P_2O_5.
1103910	1914	Willson and Haff	Phosphate rock, feldspar	Materials are fused in an electric furnace	Production of phosphoric acid and potash.

TABLE VIII.—*Processes for the production of soluble or available phosphates containing two or more fertilizer ingredients.*

Patent No.	Date.	Patentee.	Reagents used.	Treatment.	Object of patent.
16111	1856	Bickell, Charles	Feldspar, phosphate of lime, lime	Ingredients are heated together and treated with water	Products are a double silicate of aluminum and lime, phosphate of lime, lime, all insoluble in water; and caustic potash and a little caustic lime soluble in water.
26196	1859	Mapes, J. J.	Bones (100), H_2SO_4 (56), guano (36), $(NH_4)_2SO_4$ (20).	Ingredients are thoroughly mixed	Production of phosphatic nitrogenous fertilizer.
35417	1862	Harper, Louis	Nitrogenous organic matter, H_2SO_4, guano.	Allowed to stand	Restoration of guano.
39519	1863	Wilson, Geo. F	Bone sulphate (residue remaining after treatment of bones with H_2SO_4), ammonia (obtained by distillation).	Ingredients are thoroughly mixed	Production of "Binitro phosphate."
49891	1865	Klett, F.	Feldspar, carbonate or hydrate of lime, fluoride of calcium, phosphate of lime or iron.	Constituents are mixed and calcined at a red heat for about 5 hours.	Products are a soluble silicate of lime and aluminum and a phosphate of potassium or sodium.
61870	1867	Reimer, F.	Soil (16), KNO_3 (1), $(NH_4)_2SO_4$ (2), ground bone (1).	Constituents are mixed and cured	Production of an economic fertilizer.
72026	1867	Grimes, W. C.	Ground bone (8 bushels), Na_2SO_4 (80 pounds), H_2SO_4 (180 gallons), urine (40 gallons), soil (10 bushels).	Ground bone, Na_2SO_4, and H_2SO_4 are mixed. Urine and soil are added after two hours.	Production of an improved fertilizer.
77840	1868	Ramsburgh, J. S.	Bone (100), $(NH_4)_2SO_4$ (25), boiling water (3 gallons), H_2SO_4 (25 gallons), Na_2SO_4 (60 pounds), $CaSO_4$ (125 pounds), slaked lime (150 pounds), ashes.	Bones, $(NH_4)_2SO_4$, boiling water, and H_2SO_4 are mixed. While the mixture is hot Na_2SO_4, $CaSO_4$, slaked lime, and ashes are added.	Improvement in fertilizer.

TABLE VIII.—*Processes for the production of soluble or available phosphates containing two or more fertilizer ingredients*—Continued.

Patent No.	Date.	Patentee.	Reagents used.	Treatment.	Object of patent.
78730	1868	Fales, Levi S	Raw bones, leather, blood, H_2SO_4 sludge, NH_3 gas, peat or sea sand.	Materials are thoroughly mixed	Improvement in manufacture of fertilizer.
88443	1869	Burkholder & Wilson	Bone dust, oil of vitriol, Na_2SO_4, $NaNO_3$, NaCl, plaster potash, sand.	do	Improvement in fertilizers.
100457	1870	Shepard, C. U., jr	Quicklime, ammoniacal water of gas works, H_2SO_4, phosphatic material.	Quicklime is mixed with the ammoniacal water and the mixture heated. The liberated ammonia is absorbed by H_2SO_4, but not to saturation, leaving the product in a fluid state. This fluid is then poured over phosphatic material.	Production of an ammoniated superphosphate.
100729	1870	Commins, J	Gas liquor, blood, H_2SO_4, steam, phosphate rock.	Mixture is evaporated to dryness	Improvement in fertilizers.
110084	1870	Spence, Peter	Aluminum phosphate, H_2SO_4, NH_3, sawdust.	Phosphate is ground and mixed with H_2SO_4. Mixture is heated until solution is completed. NH_3 gas is run into the solution. After alum has been allowed to crystallize out, the solution is run upon sufficient sawdust to absorb it.	Production of material for the manufacture of alum and an artificial fertilizer.
124964	1872	Manwaring & Birch	Cottonseed hulls, lime, H_2O	Hulls are burned and the ashes taken up with water. Lime is added and the solution decanted.	KOH and $Ca_3(PO_4)_2$.
135995	1873	McDougall, J	Acid phosphate, sawdust, NH_3	Ammonia vapors are absorbed by acid phosphate mixed with sawdust.	Improvement in fertilizers.
206077	1878	Boykin & Carmer	Dissolved bone, plaster, $NaNO_3$, Na_2SO_4, $(NH_4)_2SO_4$, ashes, peat.	Materials are thoroughly mixed	Improved fertilizer.
246121	1881	Graf, Leopold	Liquid leather (obtained by boiling tanned scrap leather with KOH and water under pressure), gypsum, phosphate rock, H_2SO_4.	Materials are mixed and heated to drive off moisture	Do.
317010	1885	Pierce, W. S	Aluminum and iron phosphate, $(NH_4)_2SO_4$, oil of vitriol.	Phosphate and $(NH_4)_2SO_4$ are pulverized, mixed, treated with acid, and dried.	Phosphate nitrogen fertilizer.
345625	1886	Dunne, J. J	Phosphates, K_2SO_4, Na_2SO_4, coal	Mixture is roasted to a temperature just below fusion	Phosphate of potash.
353210	1886	Dudley, D. W	Bone meal (1), wood ashes (1), H_2O, lime, acid, gypsum, and NaCl.	Lime is slaked in brine, mixed with gypsum and sodium chloride, and the whole mixed with bone meal and wood ashes.	Improved fertilizer.
374201	1887	Petraeus, Carl V	Phosphate of lime, H_2SO_4, water, K_2SO_4, K_2CO_3 or KOH.	Phosphate is ground and treated with H_2SO_4. Mass is leached with water and K_2SO_4 is added to the solution. The solution is then filtered and K_2CO_3 added. On heating this solution the lime, magnesium, aluminum, and iron phosphates separate out. The remaining solution is filtered, evaporated, and cooled.	Acid phosphate of potash.
395532	1889	Williams, Wm. J	Oil of vitriol, nitrogenous matter, water, phosphate rock.	Nitrogenous matter is acidulated, phosphate rock moistened, and the two mixed.	Improved fertilizer.
396274	1889	Endemann, H	Tobacco stems, oil of vitriol, phosphate rock.	Tobacco stems are treated with oil of vitriol and the acid neutralized with phosphate rock.	Do.
404348	1889	do	do	Tobacco is treated with a mineral acid and then leached, the leachings being used to treat some basic material.	Do.
450253	1891	Reese, Jacob	Basic slag, ammonium salt	Materials are ground and mixed thoroughly	Calcareous phosphate ammonium fertilizer.

450254	1891	.....do.....	Phosphatic slag, potassium salts.....	Materials are ground and mixed.....	Production of available K_2O and P_2O_5.
450255	1891	.....do.....	Basic slag, ammonium salt, K_2O.....	.....do.....	Phosphatic nitrogenous potash fertilizer.
450531	1891	.....do.....	Basic slag, KCl.....	Materials are ground and mixed thoroughly.....	Phosphate potash fertilizer.
484631	1892	Dunne, J. J.....	Phosphate rock, nitrogenous organic matter, oil of vitriol.	Materials are mixed and dried.....	Improved nitrogen fertilizer.
535076	1895	Pieper, A. R. O.....	Aluminum phosphate, potash lye, lime.	Materials are thoroughly mixed.....	Production of citrate-soluble P_2O_5.
620443	1899	Goldsmith, W. L.....	Phosphate rock, soft coal, H_2SO_4, K, and nitrogenous matter.	Materials are mixed throughly.....	Improved fertilizer.
709185	1902	Terne, Bruno.....	Phosphate rock, oil of vitriol, NH_3 liquor.	.....do.....	Do.
731461	1903	Jarecki, A. K.....	Phosphate rock, oil of vitriol, waste beet-sugar alcohol slop, addition of absorbents or driers.	.....do.....	Fertilizer.
897695	1908	Young, J. R.....	Phosphate rock, H_2SO_4, organic ammoniates.	.....do.....	Production of ammoniated acid phosphate.
911283	1909	.....do.....	Organic ammoniates, phosphate rock, sulphuric acid, potash.	Materials are mixed.....	Production of complete fertilizer.
936317	1909	Halvorsen, B. F.....	Phosphate rock, HNO_3, $Ca(NO_3)_2$.	Phosphate rock is dissolved in HNO_3 and the excess of moisture taken up with calcined $Ca(NO_3)_2$.	Production of solid fertilizer containing P_2O_5 and N.
988894	1911	Peacock, Samuel.....	Commercial calcium cyanamid, phosphoric acid.	Cyanamid is intimately and rapidly mixed with phosphoric acid, temperature not to rise above 150° C.	Mixture of calcium phosphate and calcium cyanamid.
1001350	1911	Caro & Scheele.....	H_3PO_4, H_2SO_4, NH_3.....	NH_3 gas passed into H_3PO_4.....	Stable nonhygroscopic ammoniated superphosphate.
1020293	1912	Klingbiel, Carl.....	Solution of acid sodium phosphate, KCl, NH_3, HCl.	KCl is introduced in the solution of acid sodium phosphate, and the solution is boiled. Potassium phosphate is procured by repeated boiling and crystallization. For the manufacture of $NH_4H_2PO_4$, the acid sodium phosphate solution is neutralized with NH_3 gas. The precipitate is filtered off and HCl added to the filtrate.	Production of potassium or ammonium phosphate.
1036909	1912	Saarbach, Ludwig.....	Mineral phosphates containing carbonates, nitrogen oxides, moisture.	Phosphate is exposed to nitrogen oxides in presence of moisture.	Production of available phosphoric acid and calcium nitrate or nitrite or both.
1040081	1912	Willson, T. L., and Haff, M. M.	Monocalcic phosphate, ammonia gas..	Ammonia is introduced into the damp or pasty mass of monocalcic phosphate.	Production of dry nitrogenous phosphatic fertilizer.
1057876	1913	Peacock, Samuel.....	Phosphate rock, gases or vapors containing nitric acid, water.	Phosphate is ground and immersed in water. Nitric acid gases are led in.	Production of material containing calcium nitrate and dicalcium phosphate.
1058037	1913	Collett, Emil.....	Phosphate of lime, dilute HNO_3, sulphate of ammonia, ammonia, or carbonate of ammonia.	Phosphate is dissolved in dilute HNO_3. Sulphate of ammonia is added to precipitate lime as sulphate. Solution is separated from precipitate and neutralized with ammonium or carbonate of ammonium. It is then evaporated until crystallization takes place.	Production of phosphate and nitrate of ammonia.
1058145	1913	Braun, F. W.....	Phosphate rock which consists principally of tricalcic phosphate and calcium carbonate, HNO_3.	Phosphate rock is ground and mixed with HNO_3.....	Production of a fertilizer containing monocalcic phosphate and calcium nitrate.
1062869	1913	Willson, T. L., and Haff, M. M.	Superphosphate, NH_3, nitric oxide...	NH_3 is introduced into superphosphate. Acid superphosphate is added to neutralize any free NH_3. Nitric oxide may be added.	Nitrogen-containing phosphate.

TABLE VIII.—*Processes for the production of soluble or available phosphates containing two or more fertilizer ingredients*—Continued.

Patent No.	Date.	Patentee.	Reagents used.	Treatment.	Object of patent.
1099151	1914	Nicholas, F. C.	$CaSO_4$, phosphate rock, bitumen, and potash-bearing silicates.	Materials are mixed	Production of available P_2O_5 and K_2O.
1100638	1914	Washburn, F. S.	Phosphate rock, H_2SO_4, NH_3	Phosphate rock is treated with an excess of H_2SO_4. The resulting solution is treated with NH_3.	Production of soluble NH_3 and P_2O_5.
1103115	1914	do	Crude H_3PO_4, solution of $NH_4H_2PO_4$, and $(NH_4)_2HPO_4$.	Materials are mixed	Production of a nitrogenous and phosphatic fertilizer.
1112183	1914	Willson, T. L., and Haff, M. M.	Double superphosphate, NH_3 gas	Double superphosphate is treated with NH_3 gas	A dry nitrogenous phosphate fertilizer.
1122183	1914	do	Superphosphate, NH_3 gas	Damp pasty superphosphate is treated with dry NH_3 gas	Production of a nitrogenous phosphate fertilizer.

TABLE IX.—*Processes for the production of soluble phosphate by electrolysis.*

Patent No.	Date.	Patentee	Reagents used.	Treatment.	Object of process.
669271	1901	Denbergh, F. P. Van	Apatite, etc., siliceous flux, electric current, oxygen, steam or water vapor.	Apatite is crushed and together with the flux is placed in an electric furnace. Phosphorus is liberated by electrolysis in an atmosphere containing an excess of oxygen. The resultant P_2O_5 is hydrated by leading steam into the furnace.	Method of producing pure phosphoric acid.
707886	1902	Wiborgh, J. G., and Palmaer, W.	Apatite or other mineral phosphate, a salt of such composition that during electrolysis an acid which forms a soluble salt with lime and a basic hydrate are formed, water, electricity.	Salt solution is the electrolyte. Phosphate is placed in the solution near the anode. Calcium phosphate is precipitated at cathode end, collected, and dried.	Production of citrate-soluble phosphate.
748523	1903	Palmaer, Wilhelm	Salt solution as above, mineral phosphate, CO_2.	During electrolysis the acid and alkaline solutions are drawn off separately. The acid solution is made to act on phosphate in a separate vessel. The alkaline solution is added until the acid reaction disappears, bicalcic phosphate being precipitated. The filtrate is mixed with the rest of the cathode solution and CO_2 led in. This precipitates the lime and regenerates the electrolyte.	Method of producing bicalcic phosphate.
819410	1906	Clemm, Adolf	Mineral phosphate or bones, etc., HCl, electricity.	Phosphate is treated with HCl. The solution is separated from the residue and neutralized. It is then electrolyzed, chlorine being evolved at the anode and hydrogen at the cathode. At the cathode a precipitate of $Ca_2H_2P_2O_8$ is formed.	Production of chlorine and citrate-soluble phosphate.

TABLE X.—*Processes for the enrichment of phosphates.*

Patent No.	Date.	Patentee.	Reagents used.	Treatment.	Object of process.
86574	1869	Ottolengin, A. M	Water or air, phosphate rock	Phosphate is ground under water and heavier particles separated by difference of specific gravity.	Method of concentrating phosphate rock.
789647	1905	Arens, Richard	Water, superphosphate, heat, calcium bisulphite solution containing phosphate (formed by treating tricalcium phosphate with sulphurous acid).	Superphosphate is leached with water, giving a solution of monobasic calcium phosphate. This solution is heated and the calcium bisulphite solution run into it. Sulphurous acid is given off and collected.	Production of dibasic calcium phosphate free from sulphurous acid.
971830	1910	Coates, L. R	Mineral which is composed of phosphate and carbonate of lime and phosphatic fossils, heat, air.	Mineral is burned and slaked by exposure to air. The material is then screened, and the coarser particles (largely lime phosphate) are ground and added in predetermined proportion to the material that has passed the screen.	Process of unification and enrichment.
1014254	1912	Pratt, N. P	Earthy deposits consisting of phosphate of lime and calcium sulphate, saline solution, such as sea water.	Earthy material is treated with sea water, which dissolves the calcium sulphate, leaving behind the phosphatic material in a porous condition.	Process of enrichment.
1014255	1912	do	Acid phosphate or other phosphate containing sulphate, suitable solvents, such as water or sea water, etc.	Phosphate is treated with a solvent which dissolves the sulphates, leaving the phosphate behind.	Do.

TABLE XI.—*Processes and apparatus for the mechanical treatment of phosphate rock and soluble phosphates.*

Patent No.	Date.	Patentee.	Reagents used.	Treatment.	Object of process or apparatus.
75330	1868	Wilson, G. F	Steam or hot air, acid phosphate	Acid phosphate is exposed in thin sheets and steam or hot air passed over it.	Production of dry acid phosphate.
75331	1868	do	Acid phosphate, screening	Acid phosphate is put through screens	Separation of coarse from fine material.
75332	1868	do	Bones, furnace for burning same	Bones are placed in a special form of furnace and burned to whiteness.	Production of colorles s bone ash.
75333	1868	do	Acid phosphate, mill for disintegrating.	The acid phosphate is disintegrated in a special form of mill in such a way as not to heat the acid phosphate.	Production of pulverulent acid phosphate.
75334	1868	do	Acid phosphate, grinding and screening.	The acid phosphate is granulated in a special mill and passed through screens.	Production of finely pulverized acid phosphate.
75335	1868	do	Acid phosphate, lead and gutta-percha pump.	The acid phosphate is conveyed by a pump made of lead and gutta-percha.	Form of noncorrosive pump for acid-phosphate liquor.
75337	1868	Wilson, G. F., and Horsford, E. M.	Acid phosphate, farinaceous material, drying platforms, heat.	The acid phosphate is mixed with farinaceous material and spread on drying platforms having a temperature of 75° F.	Production of dry acid phosphate.
86289	1869	Duvall, A	Phosphate rock, H_2SO_4, steam blast	The phosphatic material and H_2SO_4 are mixed by blowing a blast of steam against the materials as they issue from a spout.	Apparatus for mixing H_2SO_4 with pulverized phosphate rock.

TABLE XI.—*Processes and apparatus for the mechanical treatment of phosphatic rock and soluble phosphates*—Continued.

Patent No.	Date.	Patentee.	Reagents used.	Treatment.	Object of process or apparatus.
102648	1870	Baugh, E. P.	Guano or acid phosphate, spread on series of gratings, through which hot air is passed.	Guano or acid phosphate is spread in layers over a series of gratings, through which hot air is passed.	Production of dry phosphatic fertilizer.
105319	1870	Duvall, A.	Acid phosphate, special form of bin.	After mixing the acid and phosphate rock the product is discharged into a special form of bin.	Production of a better acid phosphate.
106147	1870	Frank & Adt	Acid phosphate and cylindrical drier.	Acid phosphate is put through a special form of cylinder dryer.	Production of dry acid phosphate.
114693	1871	Lewis, Geo. T.	Phosphate rock, water, grinding mill.	The phosphate rock is ground in a mill with water.	Improvement in method of grinding phosphate.
335673	1886	Bacon, E. C.	Phosphate rock, washing machine.	The phosphate rock is washed in a special form of machine. (1 illustration.)	Improvement in method of washing phosphate rock.

TABLE XII.—*Production of soluble or available phosphates by miscellaneous processes.*

Patent No.	Date.	Patentee.	Reagents used.	Treatment.	Object of patent.
54635	1866	Wister, J.	Bones, gypsum	The ingredients are thoroughly mixed and ground	The gypsum facilitates grinding.
67335	1867	Moore, J. H.	Oyster or clam shells, H_2SO_4	The shells are ground and mixed with H_2SO_4 as in the manufacture of acid phosphate.	Soluble fertilizer.
71856	1876	Ravenel, St. J.	Phosphate rock, iron pyrites	The ingredients are ground and thoroughly mixed and allowed to weather.	The gradual formation of soluble phosphates.
209980	1878	Pirz, A.	Powdered bone, $CaSO_4$	Ingredients are thoroughly mixed with water	Production of available P_2O_5.
238133	1881	Lewis, Geo. T.	Phosphate rock, coarsely broken pyrites.	Ingredients are thoroughly mixed and exposed to weather for several months.	Do.
241868	1881	Liebig, G. A.	Phosphate rock, carbon, heat	Ingredients are thoroughly mixed and submitted to high heat.	Do.
423320	1890	Hodgkins, E. R.	Phosphate rock, CaO, water	The phosphate rock is finely ground and piled in alternate layers with CaO. The whole is sprinkled with water.	Do.
453749	1891	Van Ruymbeki, J.	Aluminum phosphate, "stick," $CaCO_3$.	Phosphate rock and $CaCO_3$ are thoroughly mixed with "stick" liquor.	Production of dry product containing available P_2O_5.
493889	1893	Gordale, S. L.	Hydrated phosphates of iron and aluminum.	Mixture is heated to 275° to 325° C. and allowed to cool	Production of available P_2O_5.
517661	1894	Powter, N. B.	Aluminum phosphate and slaughter-house refuse.	Ingredients are thoroughly ground and mixed	Production of fertilizer.
517662	1894	.....do	.....do	.....do	Process of making fertilizer described in Patent No. 5171.

714330	1902	Reese, Jacob.....	Phosphate rock, oxides of iron and manganese, heat.	Ingredients are mixed and heated in presence of oxidizing flame.	Production of citric-soluble phosphate.
789440	1905	Machalske, F. J.....	Phosphate rock, NaCl, C, N, Na_2CO_3, heat.	A mixture of phosphate rock and NaCl is fused in an atmosphere of N. PCl_5 is led off and the residue fused with Na_2CO_3.	Production of PCl_2 and $Na_2C_2N_2$.
792314	1905	Chisolm, Wm. B.....	Phosphate rock, sulphur, CaO, water...	A mixture of sulphur, lime, and water is first heated until the mass is homogeneous. This is mixed with phosphate rock and the whole dried and ground.	Production of available P_2O_5.
824280	1906	.....do.....	Phosphate rock, sulphur, N or K bearing materials.	Phosphate rock and sulphur are intimately mixed and ground. Nitrogen or potash bearing materials are added.	Production of fertilizer containing available P_2O_5.
824281	1906	.....do.....	Phosphate rock, sulphur, grinding.....	Phosphate rock and sulphur are first roughly crushed and then passed into a mill, where they are finely ground.	Process of preparing mixture for fertilizer described in Patent No. 824280.
947795	1910	Coates, L. R.....	Sterilized culture mixture, breaking-down-rock containing microorganisms, some food for bacteria, phosphate rock.	Breaking-down rock is added to culture mixture, giving culture which causes rock decay; sterilized ground bone and sterilized phosphate rock are added.	Production of available P_2O_5 and K_2O from insoluble minerals.
1002143	1911	Frerichs, F. W.....	Phosphate rock $(NH_4)_2SO_4$, heat, water.	Phosphate rock and $(NH_4)_2SO_4$ are mixed and roasted till a temperature of 500° C. is attained. NH_3 and H_2O escape and a mixture of calcium metaphosphate and $CaSO_4$ remains in retort. This is treated with water.	Production of calcium metaphosphate and ammonia.
1002248	1911	Ellis, Carleton.....	Phosphate rock or basic slag, humus or peat, borax waste, lime, saccharine material, nitrogen-assimilating bacteria cultures, heat.	The humus or peat is first sterilized by heat or borax waste. It is then mixed with phosphate rock; lime and material containing nitrifying bacteria are added. Saccharine material may be added to aid growth of bacteria.	Production of available P_2O_5 and process of producing same.
1032763	1912	Newberry, S. B., and Barrett, H. M.	Phosphate rock, carbon, heat, air.....	Phosphate rock and carbon are ground and mixed. The mixture is then strongly heated, first in reducing atmosphere and then in oxidizing flames. Product is ground.	Production of citrate-soluble P_2O_5.

ADDITIONAL COPIES

OF THIS PUBLICATION MAY BE PROCURED FROM
THE SUPERINTENDENT OF DOCUMENTS
GOVERNMENT PRINTING OFFICE
WASHINGTON, D. C.
AT
5 CENTS PER COPY

▽